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CHEMISTRY.

BY

J. MURRAY,

LECTURER ON CHEMISTRY, AND ON MATERIA MEDICA
AND PHARMACY, EDINBURGH.

IN FOUR VOLUMES.

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CONTENTS OF VOL. II.

Part II. OF THE CHEMICAL PROPERTIES AND COMBINATIONS OF INDIVIDUAL SUBSTANCES,—TABLE OF CLASSIFICATION. Page 1

Book I. OF ATMOSPHERIC AIR AND ITS ELEMENTS. 17

Chap. I. OF OXYGEN GAS, - - 19
II. OF NITROGEN GAS, - - 29
III. OF ATMOSPHERIC AIR, - 39
IV. OF THE CHEMICAL AGENCY OF OXYGEN IN ITS PURE FORM, AND AS IT EXISTS IN ATMOSPHERIC AIR, - 60

Book II. OF WATER AND ITS BASE. 101

Chap. I. OF HYDROGEN, - - - 102
II. OF WATER, - - - 115

Book III. OF ALKALIS AND THEIR BASES. 160

Chap. I. OF AMMONIA AND ITS BASE, - 165
II. OF POTASSA AND ITS BASE, - - 180
III. OF SODA AND ITS BASE, - - 201

Book IV. Of Earths and their Bases. 213

Chap. I. Of Barytes and its Base, - 222
II. Of Strontites and its Base, - 232
III. Of Lime and its Base, - - 236
IV. Of Magnesia and its Base, - 243
V. Of Argil and its Base, - 247
VI. Of Silex and its Base, - 259
VII. Of Zircon and its Base, - 272
VIII. Of Glucine and its Base, - 274
IX. Of Ittria and its Base, - - 275

Book V. Of Acids and their Bases. 278

Chap. I. Of Nitric Acid and the Combinations of its Base with Oxygen, - - 292

Sect. 1. *Of Nitric Acid,* - - 293
2. *Of Nitrous Acid,* - - 321
3. *Of Nitric Oxide,* - - 328
4. *Of Nitrous Oxide,* - - 349

Chap. II. Of Sulphuric Acid and its Base, 364

Sect. 1. *Of Sulphur,* - - 365
2. *Of Sulphuric Acid,* - - 371
3. *Of Sulphurous Acid,* - - 405
4. *Of Sulphuretted Hydrogen and other Compounds of Sulphur and Hydrogen,* - 413
5. *Of the Compounds of Sulphur with the Alkalis and Earths.* - - - 452

Chap. III. Of Carbonic Acid and its Base, 455

Sect. 1. *Of Diamond,* - - - 457
2. *Of Plumbago,* - - - 467
3. *Of Charcoal,* - - - 471
4. *Of Carbonic Acid,* - - 498

Sect. 10. *Of the Amniotic Fluid*, - Page 659
11. *Of the Humours of the Eye*, - 661
12. *Of Muscular Fibre*, - 663
13. *Of Skin, Cellular Fibre, and Membrane*, 672
14. *Of Tendon, Ligament, Cartilage, Horn, Hair, &c.* - - 676
15. *Of Bone and Shell*, - 686
16. *Of Fat, Spermaceti, Sebacic Acid*, 699
17. *Of the Cerebral Pulp*, - 706

Chap. III. OF THE DECOMPOSITION OF ANIMAL SUBSTANCES FROM THE RE-ACTION OF THEIR ELEMENTS, - - 708

Sect. 1. *Of the Decomposition of Animal Substances at a high temperature. Prussic Acid*, - 709
2. *Of the Spontaneous Decomposition of Animal Substances at low temperatures. Putrefaction*, 725

SYSTEM

OF

CHEMISTRY.

PART II.

OF THE CHEMICAL PROPERTIES AND COMBINATIONS OF INDIVIDUAL SUBSTANCES.

HAVING considered the operation of those general forces, from the exertion of which the phenomena of chemistry arise, we are prepared to enter on the remaining part of the science,—that which relates to the chemical properties and combinations of individual substances. In proceeding to this, I have first to present the outline of the order in which they may be arranged.

The great object of chemistry is to trace the combinations of matter; to discover what bodies are compound; by pursuing the steps of analysis, to arrive, if possible, at the knowledge of their ultimate principles or real elements; and to establish with certainty the chemical constitution of their compounds. Chemistry will have arrived at perfection, when this (if it ever should be) has been attained.

In framing systems of chemical arrangement, these ultimate objects have generally been kept in view, and the arrangement has often been formed as if they had been attained. The substances which remain, as the ultimate products of analysis, have been regarded as simple; they have formed the basis of classification; and from this the compounds resulting from their combination have been arranged in a determinate series, including all existing substances.

I have pointed out in the preface to this work the imperfections of this method. The substances assumed as simple, can with no certainty be regarded as such; our methods of analysis are imperfect; and we are probably far from having attained to the knowledge of the real elements of matter. The necessary effect, therefore, of the progress of the science, is to modify and ultimately to subvert these arrangements, and thus to render them perpetually fluctuating.

I have also stated my intention of adopting an arrangement precisely the reverse of this, taking as the basis of the classification of substances, relations in their chemical properties, forming from these relations certain orders, and under the history of the substances belonging to these, tracing their composition so far as analysis has been carried; thus arriving at their more remote principles; and from these following all their combinations. The following table will shew at a glance this arrangement; and to render it more perfect, I have included the arrangement of the preceding part of the work, so as to present a view of the whole classification of the science.

TABLE OF CLASSIFICATION.

PART I.

OF THE GENERAL FORCES PRODUCTIVE OF CHEMICAL PHENOMENA.

OF ATTRACTION.

OF THE ATTRACTION OF AGGREGATION.

— CHEMICAL ATTRACTION OR AFFINITY.

OF REPULSION, AND THE POWERS BY WHICH IT IS PRODUCED.

OF CALORIC.

— LIGHT.

— ELECTRICITY AND GALVANISM.

PART II.

OF THE CHEMICAL PROPERTIES AND RELATIONS OF INDIVIDUAL SUBSTANCES.

General View of the Chemical Constitution of Bodies, and of their mutual Chemical Relations.

OF ATMOSPHERIC AIR AND ITS IMMEDIATE PRINCIPLES.

OF THE CONSTITUTION OF THE ATMOSPHERE.
— OXYGEN.
— NITROGEN.
— ATMOSPHERIC AIR.
— THE CHEMICAL AGENCY OF OXYGEN IN ITS PURE FORM, AND AS IT EXISTS IN ATMOSPHERIC AIR.

OF WATER AND ITS BASE.

OF HYDROGEN.
— WATER.

OF ALKALIS AND THEIR BASES.

OF AMMONIA AND ITS BASE.
— POTASSA AND ITS BASE.
— SODA AND ITS BASE.

OF EARTHS AND THEIR BASES.

OF BARYTES AND ITS BASE.

— STRONTITES AND ITS BASE.

— LIME AND ITS BASE.

— ARGIL AND ITS BASE.

— MAGNESIA AND ITS BASE.

— SILEX AND ITS BASE.

— ZIRCON AND ITS BASE.

— GLUCINE AND ITS BASE.

— ITTRIA AND ITS BASE.

OF ACIDS AND THEIR BASES.

OF NITRIC ACID AND ITS BASE.

OF NITRIC ACID.

— NITROUS ACID.

— NITRIC OXIDE.

— NITROUS OXIDE.

OF SULPHURIC ACID AND ITS BASE.

OF SULPHUR.

— SULPHURIC ACID.

— SULPHUROUS ACID.

— SULPHURETTED HYDROGEN.

— SULPHURETTED AND HYDRO-SULPHURETTED ALKALIS AND EARTHS.

OF CARBONIC ACID AND ITS BASE.

OF CARBON.
— CARBONIC ACID.
— CARBONIC OXIDE.
— CARBURETTED, AND OXY-CARBURETTED HYDROGEN GASES.
— CARBURETTED SULPHUR.

OF PHOSPHORIC ACID AND ITS BASE.

OF PHOSPHORUS.
— PHOSPHORIC ACID.
— PHOSPHOROUS ACID.
— PHOSPHURETTED HYDROGEN.
— PHOSPHURETTED SULPHUR.

OF MURIATIC ACID AND ITS BASE.

OF MURIATIC ACID.
— OXYMURIATIC ACID.
— HYPER-OXYMURIATIC ACID.

OF FLUORIC ACID AND ITS BASE.

OF BORACIC ACID AND ITS BASE.

OF METALS,

OF GOLD.
— SILVER.
— PLATINA.
— IRIDIUM.
— OSMIUM.
— RHODIUM.
— PALLADIUM.
— QUICKSILVER.
— COPPER.
— IRON.
— LEAD.
— TIN.
— ZINC.
— NICKEL.

OF COBALT.
— MANGANESE.
— ARSENIC.
— BISMUTH.
— ANTIMONY.
— TELLURIUM.
— CHROME.
— MOLYBDENA.
— TUNGSTEN.
— TITANIUM.
— URANIUM.
— COLUMBIUM.
— TANTALIUM.
— CERIUM.

OF THE NATIVE COMBINATIONS OF ACIDS, EARTHS, METALS AND INFLAMMABLES, MINERAL COMPOUNDS.

OF SALINE MINERALS.
— EARTHY MINERALS.
— METALLIC MINERALS.
— INFLAMMABLE MINERALS.
— THE NATURAL POSITIONS AND RELATIONS OF MINERALS, AND OF THEIR FORMATION.
— MINERAL WATERS.

OF VEGETABLE COMPOUNDS,

OF THE FORMATION OF VEGETABLE COMPOUNDS.
— THE CHEMICAL PROPERTIES AND RELATIONS OF VEGETABLE COMPOUNDS.
— THE SPONTANEOUS CHEMICAL CHANGES AND DECOMPOSITIONS OF VEGETABLE COMPOUNDS.

OF ANIMAL COMPOUNDS.

OF THE FORMATION OF ANIMAL COMPOUNDS.
— THE CHEMICAL PROPERTIES AND RELATIONS OF ANIMAL COMPOUNDS.
— THE SPONTANEOUS CHEMICAL CHANGES AND DECOMPOSITIONS OF ANIMAL COMPOUNDS.

On the details of this arrangement I do not consider it necessary to offer many observations. It must no doubt be liable to objection; for in a science, progressive as chemistry is, and of which many of the links probably remain to be discovered, no perfect classification can be formed. But that which I have adopted, places substances, I trust, according to well-defined chemical relations, and presents the truths of the science in an order, not inconvenient, nor difficult of acquisition.

It is scarcely possible to advance a step in the study of chemical combinations without a knowledge of the composition of the ATMOSPHERE, and of the properties of its immediate principles; I have therefore placed it first in the system.

A knowledge of the chemical properties and constitution of WATER is scarcely less necessary. It consists of oxygen and hydrogen. The former of these is previously arranged as a constituent of atmospheric air. Hydrogen only remains, therefore, to be described; and we have the advantage of introducing early a principle of the most extensive chemical agency, and which enters into the composition of a number of others afterwards described.

If the recent chemical discoveries be regarded as fully established, it might be contended, that, in strict propriety, there is no foundation, in a chemical system, for establishing as an Order the substances which have been named ALKALIS. Their bases have the greater number of the general metallic properties; and being compounds of these bases with oxygen, they have, under this point of view, no claim to be ranked as distinct from other metallic oxides. Independent, however, of the consideration, that it might be premature to subvert an order of chemical agents which has long been established, there are some grounds of distinction, which may afford reasons for arranging them as distinct substances. Their chemical properties are considerably different from those of metallic oxides; and their bases scarcely differ less from the substances more peculiarly denominated metals.

The same observations apply to the classification of the EARTHS as of the alkalis. In strictness it might be urged that they are metallic oxides. But it is equally true, that they have peculiar properties, which appear to form them into the series which connects the alkalis with the oxides of what are more strictly denominated metals. Both they and the alkalis will probably always remain as natural orders; and in questions of this nature, it ought to be kept in view, that the influence of the results of analysis on this natural system ought to be subordinate; for there is always the possibility that the analysis may be imperfect, and that the progress of investigation may restore the relations, or establish the limits, which at an earlier period it appeared to change.

If, however, the progress of chemistry should be unfavourable to this view, with regard to these particular substances, they will then be transferred to the class of metals, and their history be connected with that of their bases. At present, I should hesitate in making this change; and it would give rise to considerable difficulties with regard to the chemical history of other substances.

The ACIDS form a well-defined order from their chemical agencies. Pursuing the principle of the method I have followed, with each acid is connected the chemical history of its base, and of the primary combinations both of that base and of the acid with the substances previously described. The bases of the acids might have been arranged as a distinct order under the title of Primary Inflammables; but it is more strictly in conformity with the principles of the arrangement, to arrange them as I have done; and this is attended with no disadvantage.

The METALS constitute the next order. Their chemical characters are sufficiently determinate, and they occupy that place in the system, in which, from the previous description of all the active chemical bodies, their history can be rendered most complete.

I have not hesitated to form into an order the native combinations of Acids, Earths, Metals and Inflammables, or the substances denominated MINERALS. The characters of these are peculiar; so weak are their chemical agencies, that the greater number of them are rather considered as objects of natural history than of chemistry, and they are principally characterized by their natural properties. They are chemical compounds, however, and, so far at least as relates to their composition, are subjects of chemical science.

VEGETABLE and ANIMAL SUBSTANCES form the remaining orders. Their chemical constitution is very peculiar, and their characters as chemical substances are therefore well defined. It is one of the advantages of the method I have adopted, that they are placed in the classification as orders, on the same grounds as the others; while, in synthetic arrangements, they have been excluded, or admitted without being in conformity to the principles of the arrangement.

AFTER having stated this arrangement, I have, before I proceed to the chemical history of the substances placed under it, to offer some general observations on their more comprehensive chemical relations, so far as they are developed in the present state of the science.

SUBSTANCES are regarded by the chemist chiefly as they are compound, or as they are simple. The former are bodies which by chemical analysis can be resolved into two or more principles, different in their nature from each other, and from the substance which they formed by their union. The latter are bodies incapable of such a decomposition, and which therefore remain as the ultimate products of analysis. It is the object of chemistry to unfold the combinations of matter, and to resolve bodies into the elements of which they are formed.

Any speculation which can be advanced in the present state of chemistry with regard to these elements, and the influence they may have in giving origin to the varieties of matter, must be altogether vague. But in adapting our views to the knowledge which we have, we discover that some principles are much more active than others in the production of chemical properties, and are more extensive in their chemical relations.

At the dawn of philosophical chemistry, its cultivators were occupied in fixing the characters, and tracing the combinations of certain agents, then imperfectly known, but exerting important chemical actions. The different acids, the alkalis, the pure earths, and the principal metals, were thus characterized; they were distinguished from each other, the methods of obtaining them discovered, and their more important combinations made known. From the time of Homberg, Geoffroy and Boyle, to that of Bergman, these researches engaged the attention of chemists; and during this period the knowledge of these facts constituted nearly the whole of chemistry.

An important revolution in the science was effected by the discovery of a more subtle class of chemical principles,—the aërial fluids. Of these the principle denominated Oxygen is by far the most important; and the establishment of what has been named the Modern Theory of Chemistry consisted principally in the developement of its agencies and relations. Oxygen is a constituent part of the atmospheric air; it is the chief ingredient of water; it exists in almost all the varieties of vegetable and animal matter, and it is found in many of the substances which belong to the mineral kingdom. No principle, therefore, is more widely diffused, and there is none which exerts more powerful chemical affinities.

This principle, oxygen, in combining with bodies, produces often a great elevation of temperature, accompanied with the extrication of light. This constitutes the process of combustion or burning. The theory of Lavoisier consisted principally in the establishment of this important truth. He demonstrated, that the presence of oxygen is necessary to burning; that in every case of combustion the oxygen disappears by entering into combination with the combustible matter, and that it always exists in the substance formed by the combustion.

Many of the products of this combination are possessed of certain common characters. A class of chemical agents has long been established, under the title of Acids. The substances belonging to it are distinguished from others by having a sour taste, by the property of changing the blue, purple and green colours of vegetables to red, and by exerting powerful chemical actions on the alkalis, earths and metals, forming with them combinations, in which their properties are mutually neutralized.

All the products of combustion, however, have not the character of acidity. To distinguish these, the term Oxide has been introduced; and thus Oxides and Acids form two extensive orders of compounds, both formed from combinations of oxygen ; the latter being characterized by certain common qualities, the former not having any common distinction, farther than their oxygenation.

The substances which combine with oxygen,—Oxidifiable Bases as they are named, so far differ in their common properties as to be subdivided into two orders, Inflammables and Metals. The former combine readily with oxygen ; and this combination is attended with all the phenomena of combustion. The latter are likewise susceptible of this combination, but in general are not so highly combustible. They are farther distinguished from the others by an assemblage of common properties, opacity, lustre, and density, and are united with them principally by their relation to oxygen.

Under the three orders of Oxygen, Oxidifiable Bases, and Products of Oxygenation, the greater number of material substances could be arranged, and hence the relations between these constituted the principal part of chemical science.

There were, however, two very important orders of chemical agents, the Alkalis and Earths, which were excluded from this arrangement, and appeared insulated ; they were neither capable of combining with oxygen, nor did they appear to be products of oxygenation. Our views of the general system of chemical relations have been much extended by the important discovery, that these too are compounds of oxygen, being formed from this element united with bases which have the greater number of metallic properties. And the important general property of alkalinity is now proved to be, equally with that of acidity, the result of oxygenation.

In the present state of chemistry, then, OXYGEN is the principle evidently of first importance ; and the whole of the science may, by relations not very remote, be connected with its combinations.

OXIDIFIABLE SUBSTANCES, or those bodies which combine with oxygen, form an extensive class, including what may be named the Primary Inflammables, the Metals, and the Bases of the Alkalis and Earths. They are all connected by their relation to oxygen, and this impresses on them their most prominent character.

COMPOUNDS OF OXYGEN with oxidifiable substances, form the third class. There belong to it water, the acids, the alkalis, the earths, and a number of compounds distinguished by the general appellation of oxides. And under it may likewise be placed, though forming a more remote series, the substances which are formed by the union of these primary products, of which the most important are those derived from the combinations of acids, with alkalis, earths, and metallic oxides.

There still remains a fourth class of chemical substances, the COMPOUNDS OF OXIDIFIABLE BASES with each other, including all the metallic alloys, and the series of compounds which the metals form with the primary inflammables, or the inflammables with each other. Partly to this class, too, and partly to the preceding, may be referred the compounds which are formed in the vegetable and animal systems.

SUCH is the general view of the chemical relations of bodies which the present state of the science presents, and on this a synthetic arrangement might be formed. We are now perhaps on the eve of another revolution, in which these relations will be farther simplified, and in which, without subverting what has been already established, new and more comprehensive views will be introduced.

The general truths, very briefly stated in this rapid sketch, will be fully delivered under the different parts of the arrangement I have adopted. In giving the history of oxygen, for example, I shall have to state at length its agency in the process of combustion; and under the classes of alkalis, earths and acids, will be best placed the account of their distinctive properties and of their general chemical actions. But there is some advantage, before proceeding to the details of a science, to give a general view of its more comprehensive relations; and from these preliminary observations, I shall be enabled to enter with more advantage on the chemical history of individual substances.

BOOK I.

OF ATMOSPHERIC AIR, AND ITS ELEMENTS.

THE atmosphere, or that mass of invisible elastic fluid which surrounds the earth to a great height, diminishing in density as it recedes from the surface, may be regarded, under one point of view, as a collection of all those substances which are capable of existing in the aërial form at the medium temperature of the globe, and which are constantly disengaged, more or less abundantly, by the processes carrying on at the surface of the earth. These, mixed with the substances which they can hold in solution, with the water constantly evaporating, with the effluvia from animals and vegetables, with particles of coarser matter in a state of extreme mechanical division, and with the magnetic and electric fluids, light and caloric, form a vast mixture, the composition of which it is apparently impossible to determine with accuracy.

Chemical analysis has discovered, however, that in this mass there exists an elastic fluid of nearly uniform composition, with which the other substances are merely mingled; these are never in any considerable proportion, and are even seldom discoverable by the nicest chemical tests; they are only occasionally produced, or are very quickly abstracted by various natural processes, by which the purity of the atmosphere is preserved.

This elastic fluid, which forms the great mass of the inferior portion of the atmosphere, consists principally of two substances, oxygen and nitrogen, which exist naturally in the gaseous form, and of a very small portion of another gas,—carbonic acid. It has also been supposed, that as hydrogen gas, more or less pure, is constantly produced at the surface of the earth, from various chemical processes, particularly from the decomposition of animal and vegetable matter, and as, from its greater levity, it does not remain, or remains only in a very diluted state, near the surface, so as to be again absorbed or abstracted, it may form the upper stratum of the atmosphere. With regard to this we cannot decide. It is only the inferior portion of it that we can subject to examination; and it is to this elastic fluid, composed almost entirely of oxygen and nitrogen gases, that the term Atmospheric Air is in chemical language exclusively applied.

The composition of atmospheric air is discovered by experiments which present very simple results. If a measured portion of it be submitted to the chemical action of certain substances,—of phosphorus for example, or of the compound produced by boiling lime and sulphur together in water, it suffers a diminution of its volume equal nearly to one-fourth, and the air which remains has no longer the same properties; it is in particular incapable of supporting combustion, or of sustaining animal life. This is an analysis of atmospheric air. There exists an elastic fluid, oxygen gas, as it is named, which in its pure form is eminently capable of supporting combustion, and of enabling animals to live by respiration; and these properties, as possessed by atmospheric air, are owing to the presence of this principle. Hence the changes which it suffers in the above analysis. It is diminished nearly one-fourth in volume, this being the quantity of oxygen it contains, and which is abstracted by the substance by which the analysis is performed; and the residual air is no longer capable of supporting combustion or sustaining life, these being properties which it does not possess. But if there be added to it a portion of oxygen gas equal to what had been abstracted, these properties are restored, and an air is formed perfectly similar to atmospheric air. Thus, its composition is demonstrated both by analysis and synthesis, and we are led to the knowledge of these two aëriform fluids, oxygen and nitrogen gases, as its constituent principles. The history of these being delivered, we may consider with more advantage the chemical constitution and properties of atmospheric air.

CHAP. I.

OF OXYGEN GAS.

THIS very important chemical principle was discovered nearly about the same time by Priestley, Lavoisier and Scheele. In 1774, Priestley obtained it in an experiment in which he exposed red oxide of mercury to the heat excited by the concentration of the solar rays by a lens, and he observed its distinguishing property of rendering combustion vivid. Scheele in 1775 obtained it in the distillation of nitrous acid, from the decomposition of nitre by heat, and from a mixture of black oxide of manganese and sulphuric acid, and observed in it the same property. Lavoisier, from his experiments on the change which metals suffer when heated in atmospheric air, began, to use his own language, to suspect that the air of the atmosphere, or an elastic fluid contained in the air, was capable in a great many circumstances of being fixed and combined with metals; and in a memoir read before the Academy of Sciences in 1775, gave an account of an experiment, in which, by heating in a retort red oxide of mercury, he obtained an air which he observed to be possessed of peculiar properties, and in particular that of supporting combustion, inflammable bodies burning in it with an enlarged flame, and with more light than in common air. This he concluded to be an exceedingly pure portion of the air which surrounds us *. These three philosophers appear equally entitled to the honour of the discovery, though Lavoisier perhaps at first scarcely regarded it as essentially different from atmospheric air.

Different names were given to this gas. Scheele named it Fire Air, from the power which he observed it to possess, in a very eminent degree, of exciting and supporting combustion, and from supposing that it even entered into the composition of fire. Dr Priestley, from a theoretical opinion as to its nature, termed it Dephlogisticated Air, or air most completely deprived of Phlogiston, or the Principle of Inflammability. Lavoisier called it Air eminently Pure; and afterwards, finding that when breathed by animals it supported life longer than any other

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* Mémoires de l'Acad. des Sciences, 1775, p. 520.

air did, Air eminently Respirable. Condorcet imposed the more elegant appellation of Vital Air, derived from the same property, and Bergman that of Pure Air. These names, besides particular objections, are all incapable of combination, or of being employed in the formation of derivative terms. At the framing of the new nomenclature, it was necessary that a name should be invented, having this advantage; and Oxygen, derived from the Greek word ὀξυς, sour or acid, was preferred, it being a distinctive property of this substance to form combinations possessed of acidity. In conformity to the principles of the nomenclature, Oxygen denotes the solid base or gravitating matter, and Oxygen Gas is the name given to it when it exists in the aërial form. Some have supposed, that when in the gaseous state it is united, not merely with caloric, but likewise with light; but of this we have no proof; and if light be contained in it, it is probably rather combined in the particles of oxygen itself, and not peculiar to it in the aërial form.

Oxygen is a principle very generally diffused. In the state of gas it forms one-fourth part of atmospheric air; in combination it exists in water in a proportion not less than 85 in 100 parts; it is a principle of all acids, and of course of all acid combinations, and hence it is an ingredient in many saline and mineral substances; it appears to exist in the composition of the alkalis and earths; it is besides found in nature, combined with many of the metals, and it is a constituent part of the greater number, perhaps, indeed, of all vegetable and animal products It is nowhere presented to us, however, perfectly pure, and hence certain processes are requisite to obtain it in this state.

In a number of its combinations it is retained by an attraction sufficiently weak to admit of being disengaged by an elevation of temperature. In common nitre it exists in great quantity; and when this salt is exposed to a red heat in a coated glass or earthen retort, oxygen gas is disengaged; it is not, however, perfectly pure, but mixed, especially towards the end of the process, with a portion of nitrogen gas. From 1 lb. of nitre about 1200 cubic inches of oxygen gas are obtained. It can be separated by a similar process from some of its metallic combinations. By Dr Priestley it was procured from red lead, and by Lavoisier from the red oxide of mercury. The black oxide of manganese, a native production, affords it with still more facility, and in greater quantity, and it is from this substance that for common experimental purposes it is generally obtained. A quantity of this oxide in powder is put into the iron bottle, to which a metallic tube is adapted, Fig. 50. Plate VI., which terminates in a gazometer or pneumatic trough. The bottle is put into a furnace or common fire, and when the temperature is raised to a high red heat, oxygen gas begins to be disengaged, is conducted by the tube, and transmitted through the water in the gazometer or in the trough, so as to be collected in the manner which has been already described *; and by continuing and somewhat increasing the temperature, a considerable quantity of gas is expelled. Its expulsion is owing to the repulsive agency of ca-

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* Vol. i. p. 235.

loric. Black oxide of manganese is a compound of a peculiar metal, manganese, with oxygen. Within a certain range of temperature this combination is permanent; but when raised to a red heat, its principles are unequally acted on; the disposition of the oxygen to assume the elastic state is a power tending to separate it from the manganese, and when the temperature is raised to a certain point, this separation begins to take place. As it proceeds, however, the proportion of manganese to the remaining oxygen is always relatively increasing; this circumstance, in conformity to the law which has been already fully stated, adds so much to the force of its affinity to the oxygen, that the decomposition is at length put a stop to, unless the temperature be still more increased; but by no elevation of temperature whatever can the decomposition be rendered complete, the manganese always retaining a portion of oxygen combined with it, forming a substance of a brown colour, in which about 20 of oxygen in 100 parts are still combined.

The expulsion of the oxygen from these metallic combinations is much facilitated by the introduction of certain affinities, so that it can be effected by a very moderate heat. If sulphuric acid be poured on red lead, or on black oxide of manganese, oxygen gas is disengaged. Two parts of black oxide of manganese are mixed with 1½ of sulphuric acid in a glass retort. On applying the heat of a lamp to the retort, oxygen gas is expelled; and by inserting the end of the neck of the retort beneath an inverted jar, filled with water, and placed on the shelf of the pneumatic trough, the gas is collected, mixed with a vapour, which renders it somewhat opaque, but which is soon absorbed by the water. The action of the sulphuric acid in facilitating the expulsion of the oxygen is owing to the affinity it exerts. The explanation that was formerly given of its agency, was founded on the assumption that manganese combines with oxygen in two proportions, in one forming a white oxide, in another and larger proportion, a black oxide; sulphuric acid was supposed to exert a much stronger attraction to the former than to the latter: hence, when poured on the black oxide, and its agency assisted by a moderate elevation of temperature, it exerted an attraction to the white oxide sufficiently strong to disengage that excess of oxygen which the black oxide contained, and the residual mass is thus composed of the white oxide with sulphuric acid. There seems little reason to admit of the existence of these two determinate oxides, and the explanation by Berthollet of this process is more general, and probably more just. Sulphuric acid is supposed to exert an affinity to manganese, and by thus dividing the attraction it exerts to the oxygen, to weaken it so far that the tendency of this principle to assume the elastic state prevails, especially when aided by the moderate heat applied, and a portion of it escapes from combination, and passes to the state of gas. The attraction of the sulphuric acid becomes weaker, however, in proportion as it enters into combination, and at length the reciprocal affinities of the manganese, the acid, and the remaining oxygen, are balanced, and a ternary compound is formed.

When oxygen gas is wished to be procured in the state of greatest purity for more delicate experimental investigations, the substance that has been employed to afford it is a salt named oxymuriate of potassa. One half of its weight consists of oxygen; it contains no other principle which, at a red heat, can be disengaged, so as to assume the aërial form; while, by such a heat, applied to it in a glass retort, the oxygen is expelled with facility; and, by rejecting the first portions that pass off, as being mixed with the atmospheric air of the vessel, it may be collected pure.

Oxygen gas is likewise yielded by growing vegetables exposed to the rays of the sun, and even in small quantity from the leaves of plants laid on the surface of water, and exposed to the solar light.

Oxygen gas is colourless, and consequently invisible; it is destitute of smell or taste; it is rather heavier than atmospheric air; its specific gravity, referred to that of water as 0.1000, is .001356; or referring it to atmospheric air, it is, according to Kirwan, 1103, to Lavoisier, 1102, and to Davy 1127. 100 cubic inches weigh, according to Mr Davy, at the temperature of 55°, and the barometrical pressure of 30, 35.06 grains.

This gas is absorbed by water, but in a quantity so inconsiderable that any diminution in its volume from agitation with that fluid is scarcely perceptible. Dr Henry has shewn that 100 cubic inches of water, freed from air by boiling, absorb of oxygen gas exposed to it, for several hours, and frequently agitated, under a common atmospheric pressure, and at the temperature of 60°, 3.55 cubic inches *. By increasing the pressure, a larger quantity was absorbed, proportioned to the pressure applied;

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* Philosophical Transactions, 1803.

and, from the experiments of Paul of Geneva it appears, that, under a great pressure, water may be made to take up about half its bulk of the gas, acquiring, however, from this impregnation, no taste or smell. This gas has also always a portion of water in the state of vapour, combined or diffused, the quantity of which it is not easy to estimate with precision.

The most characteristic property of oxygen gas, is its power of exciting and supporting combustion. When an inflammable body is kindled and introduced into it, the combustion is rapid and vivid; the combustible body burns longer, and at the same time is more quickly consumed, and much more heat and light are evolved in a given time, than when it burns in atmospheric air. The flame of a taper is enlarged and becomes dazzlingly bright; other combustibles, as sulphur, charcoal, or phosphorus, burn with splendour; and even some which do not suffer combustion, when raised to a red heat in atmospheric air, as iron, burn rapidly when they are at this temperature immersed in oxygen gas. Strictly speaking, it is indeed the only gas that supports combustion, atmospheric air and others doing so only from the oxygen they contain. During the burning, the oxygen is consumed, or is absorbed by the burning body; and hence a given quantity of it can support the process only for a limited time. The result of the combustion is frequently the production of a substance having acid properties; and the power of communicating such properties to its combinations, appears to belong exclusively to oxygen.

Oxygen gas is also distinguished by its power of supporting animal life. If an animal be confined in a given quantity of it, instead of being immediately killed, as it would be in many gases, it lives even for a longer time than it would do in the same volume of atmospheric air. A quantity of it disappears, or is consumed during respiration; a due supply of it by the lungs is indispensable to the continuance of life; and atmospheric air, or any gas, sustains life, only from the oxygen it contains and is capable of affording to the blood. This fluid, when exposed to oxygen, becomes of a florid red; a change of colour which it also suffers in the lungs. At the same time, pure oxygen does not appear to be well adapted to animal existence. If an animal be confined in a given quantity of it, its respiration becomes hurried and laborious before the whole of the oxygen is consumed, and it dies even though so much oxygen is still present, that another animal of the same species, introduced into the residual air, will live. It has been concluded from this fact, that oxygen proves too highly stimulating, and hence the necessity of an atmosphere such as ours is, in which oxygen is diluted with another air, which appears to be nearly negative in its effects.

By these two properties, that of exciting combustion, and that of supporting, by respiration, animal life, oxygen gas is peculiarly characterized.

From the former property it has been applied, as has been already observed, to excite combustion so as to obtain a very intense heat, a stream of oxygen issuing by a tube with a small aperture, from a gazometer, being directed on the flame of a lamp, or with still more effect on a piece of ignited charcoal. By this heat, platina is instantly fused, gold and silver volatilized, the other metals enter into combustion with various coloured flames, the compound earths and stones are vitrified, the gems lose their colours, and the diamond is made to burn *.

Oxygen has a tendency to combination, more extensive perhaps than any other chemical agent has. It is necessary to support combustion, and during that process it combines with the combustible body. The products are consequently compounds of oxygen, and these compounds are numerous and important agents in chemistry. The acids are of this kind, and their activity is principally dependent on their oxygen, which they yield readily to other bodies, and which, by the dense state in which it exists, is often capable of exerting powerful affinities. All the metals, too, are capable of combining with this principle, from which a number of compounds are formed. And it exists in an immense number of natural substances. With the exception of metals, and two or three inflammable substances, it now appears, indeed, that it would be difficult to select a substance in which it is not contained. It is unquestionably more abundant in nature, and more extensively diffused than any simple substance; its affinities are more numerous and more energetic; the developement of its agencies formed the principal part of what has been named the modern theory of chemistry, and still affords the most important relations of the science.

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* Mémoires de l'Acad. des Sciences, 1782, 1783.

CHAP. II.

OF NITROGEN GAS.

WHEN the oxygen gas of atmospheric air has been abstracted, there remains an elastic fluid equal in volume to more than three-fourths of the air which had been analysed. The gas has been designated by the appellation of Azote, or of Nitrogen. It is rather singular, that the first of these names should have been preferred, and been established even in general use. Derived from *α privative*, and ζωὴ *life*, it implies that the gas is incapable of sustaining, or that it proves noxious to life; but this property, so far from being peculiar to it, belongs to nearly all the aëriform fluids, and to many of them in a more eminent degree than to this one, and therefore ought not to have been made the basis of a distinctive name. A primary principle of the modern nomenclature, too, is, that the names of the compounds which any simple substance forms with oxygen, should be derived from the name of that substance. The combinations of this gas, with that principle, have been long known by the epithet Nitrous, which the framers of the new nomenclature could not change; and hence by adopting Azote as the name of the base, they violated unnecessarily the principles by which they professed to be guided. The term Nitrogen, proposed by Chaptal, is unexceptionable, and it accords with the principles of the nomenclature, in affording the radicle from which the established names of its compounds with oxygen may be derived. Other appellations have been given to this gas. It was named by Dr Priestley Phlogisticated Air; Foul or Corrupted air by Scheele; and Mephitic air at one period by Lavoisier; but these have properly fallen into disuse.

Nitrogen gas had been observed to remain after the process of combustion had been carried on in a limited quantity of atmospheric air. But being frequently mixed with aëriform products of that process, and approaching in its properties to another gas, Carbonic Acid, the Fixed Air of the older chemists, its distinctive properties had not been accurately observed, nor its existence as a peculiar substance recognised. The difference in its properties from those of fixed air, seems to have been first taken notice of by Dr Rutherford and Dr Priestley, nearly about the same time, 1772; and Scheele, who in 1775 had made the same observation, concluded that it was a peculiar kind of air, a constituent part of the atmosphere, and not, as had been supposed, atmospheric air vitiated by the processes in which it is obtained. Lavoisier drew the same conclusion from his own experiments *, though without pointing out so clearly its existence as a peculiar substance, or its characteristic properties.

It is from atmospheric air that this gas is generally procured, some substance being introduced which is capable of combining with the oxygen of the atmosphere. The

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* Physical Essays, p. 339, 340. Mémoires de l'Acad. des Sciences, 1776, p. 679.

easiest process is to kindle a bit of phosphorus in a jar containing atmospheric air ; the proportion of phosphorus being at least half a grain to a cubic inch of gas : in the combustion of the phosphorus the oxygen is consumed ; the residual air is nitrogen, mixed with a quantity of vapour from the burning of the phosphorus, which renders it opaque, but which is soon absorbed by the water over which the experiment is made, leaving the gas transparent and invisible. This nitrogen is not, however, perfectly pure : it is proved, that the burning of the phosphorus ceases before the oxygen is entirely consumed ; a part therefore remains in the gas ; and nitrogen gas appears also to have the property of dissolving a small portion of phosphorus. Other substances may be used, which will abstract the oxygen more completely : a mixture of iron-filings and sulphur, moistened with water, has this effect ; it was found by Priestley, however, that such a mixture, after some time, gives out a small quantity of hydrogen gas, with which of course the nitrogen may be mixed. The solution obtained by boiling sulphur, with a solution of potassa, or with lime and water, affords, on the whole, the best mode of procuring pure nitrogen gas. One part of it is inclosed in a bottle or tube, with 5 or 6 parts, by measure, of atmospheric air ; they are frequently agitated, and the vessel being inverted in a portion of the liquor, the air is exposed to its action until it suffer no further diminution of volume. By this liquid the whole of the oxygen of the atmospheric air is absorbed ; nothing is added to the remaining nitrogen gas, which is therefore obtained pure ; at least by agitating it with a little water, a slight fœtid odour which it acquires from the liquid, and which might be supposed to denote some impurity, is removed, without any sensible diminution in its volume.

There are other processes by which this gas may likewise be procured. It is a constituent principle of animal matter. If a few pieces of flesh or muscular fibre be put into a retort, and nitric acid previously diluted with 4 or 5 parts of water be added, on applying a moderate heat, nitrogen gas is disengaged and may be collected. Though it is an ingredient in the acid as well as in the animal matter, yet that it is evolved from the latter, is proved by its being ascertained, that none of the acid is lost or decomposed, and it appears to operate in the disengagement of the nitrogen, by the affinities it causes to be exerted among the elements of the animal matter. There is reason to believe, however, that the gas obtained in this process is not perfectly pure, but holds a little carbon dissolved.

Nitrogen gas is permanently elastic, invisible, insipid, and inodorous. It is lighter than either oxygen gas or atmospheric air, its specific gravity being to that of the latter, according to Lavoisier and Davy, as 966 to 1000; according to Kirwan as 985; to that of water as 1.0000, it is .001189; 100 cubic inches of it weigh, according to Mr Davy, at the temperature of 55, and the barometrical pressure of 30, 30.40 grains.

This gas has no very striking property, physical or chemical, by which it can be characterized: it is distinguished rather by negative qualities.

1st, It is incapable of supporting combustion; a burning body immersed in it is instantly extinguished.

2d, It is equally incapable of sustaining animal life by respiration. An animal put into a jar of it is immediately killed.

3d, It is not inflammable, or it cannot be made to burn. It is true, however, that it combines with oxygen gas, but this combination is not analogous in the phenomena it presents, to the combination of combustible bodies with that principle. It takes place very slowly, even when aided by the agency of an ignited or an electric spark; and during the combination no light is disengaged, nor is there any sensible heat produced. Hence the process cannot be termed Combustion.

Lastly, Nitrogen gas is not sensibly absorbed by water. If a jar filled with it be placed in water, it suffers no sensible diminution of volume. Mr Henry, however, has found, that when it is exposed for some hours to water, freed from the portion of atmospheric air which it holds dissolved, 100 cubic inches absorb at the temperature of 60°, and under the usual atmospheric pressure, 1.47 cubic inches.

As affording the best method of distinguishing nitrogen gas, from other gases which resemble it in general properties, it may be added, that it produces no change on the vegetable colours; and that, when agitated with lime-water, it does not render it milky, nor is it absorbed by it in larger quantity than by pure water.

Nitrogen exhibits more distinctive characters in the combinations into which it enters. It unites with oxygen in different proportions, forming compounds extremely different in their properties. It combines with hydrogen, and dissolves small portions of phosphorus, sulphur, and carbon; and, lastly, it is an element in all the products of the animal system ; it is the one which is most peculiar to them, and which perhaps give them their characteristic properties as animal substances. In its gaseous form, it does not however exert very energetic affinities, and the large quantity of it in the atmosphere seems principally to dilute the oxygen gas.

The opinions of chemists have frequently varied with regard to the nature of nitrogen. In the modern chemical system it was regarded as a simple substance. At an early period, however, some striking experiments were made by Dr Priestley, in which, by distilling water from earthen retorts, or through earthen tubes kept at a high temperature, a large quantity of aëriform fluid was procured ; and this air appeared to be principally nitrogen, with a proportion, rather variable, of oxygen. He at first concluded, that in these experiments the water is converted into air ; and a similar opinion was afterwards advanced, and attempted to be supported, by experiments of the same nature by some of the German chemists, particularly Westrumb, Wiegleb and Goettling ; nitrogen gas in their system being regarded as a compound of water and caloric, and water being the ponderable base of this as well as of the other gases.

Dr Priestley had observed, however, a number of facts adverse to the opinion he had first maintained, particularly, that when water is distilled from or through glass or metallic vessels, there is no production of air, not even when clay or fragments of the earthen ware which he had used in the first experiments were introduced into the vessel. From this it appeared to follow, that neither the earthen ware, nor the heat applied, had any share in the apparent conversion of water into air; and he concluded, that the appearance of this was owing to the porosity of earthen ware retorts or tubes, in consequence of which the watery vapour escapes, and the external air enters *,—a conclusion undoubtedly involving some difficulties, but which, on the whole, appeared to be the most probable one. It appeared also to be confirmed by subsequent experiments of Deiman and of Von Hauch.

Girtanner, however, still maintained the opinion of nitrogen being a compound. This had been suggested to him by finding it appear and disappear in many experiments, without being able to account for this, on the supposition that it is a simple body. His attention was again called to the subject, by the dispute with regard to the apparent conversion of water into nitrogen gas; he instituted a number of experiments, many of them similar to those which had been before performed, in which nitrogen was produced when water is boiled or passed through tubes; and he affirmed, in opposition to the experiments of Priestley, that this production of nitrogen takes place when the water is boiled from a glass retort, or through a heated glass tube, in either of which a little clay, lime, or siliceous earths is put. The effect is equally obtained when an earthen retort or tube is used glazed externally, but not if the glazing is on the internal surface. In all these experiments, therefore, water appeared to be converted into nitrogen gas when submitted to the action of clay and other earths at a high temperature. Girtanner adds, that having satisfied himself of the truth of the

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* Philosophical Transactions, vol. lxxiii.

fact stated by Von Humboldt and others, that the earths moistened absorb oxygen, and that they do so more rapidly at a high temperature, their agency in converting water into nitrogen probably depends on this. He therefore adopted a conclusion, which had been advanced some years before as a conjecture by Mayer, that nitrogen is a compound of oxygen and hydrogen, and that it differs from water in containing less oxygen. Atmospheric air he regarded as a compound of oxygen and hydrogen; and in the processes in which the atmospheric air appears to be analysed, part of the oxygen he supposes to be abstracted, and the remaining quantity brought into combination with the hydrogen, so as to form nitrogen gas. Nitrogen, the nitrous compounds, atmospheric air, water, and ammonia, according to this system, consist of the same elements in different proportions *.

With these conclusions Girtanner connected several others, such as that muriatic acid and the fixed alkalis are similar compounds, and, proceeding to the ultimate elements of matter, that oxygen and hydrogen are those of which all bodies are formed. These apparently extravagant speculations, and unfounded assertions, threw discredit on his opinions. The accuracy of his experiments too were called in question, particularly by Berthollet and Lagrange, who repeated the greater number of them without obtaining the results which had been described †.

There is another class of facts from which the existence of a peculiar relation between nitrogen and water was

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* Nicholson's Journal, 4to, vol. iv. p. 137, &c.

† Ibid. p. 371.

supposed to be established. Dr Priestley had observed, that when water had been freed as completely as possible from any air which it might be supposed to hold dissolved, by the air-pump, or by any other methods, still on converting it into vapour, a little permanent elastic fluid is disengaged, which he found to be nitrogen; and this continued to be formed as long as he continued the experiment. This led him to examine the air which is disengaged from water in freezing. Having exposed, therefore, to a sufficient degree of cold, water which by repeated processes with the Torricellian vacuum had been as completely deprived of air as possible, he found, that the ice into which it was converted, though transparent on the outside, was opaque towards the centre; and when again melted, many small bubbles of air were disengaged from it. And when the freezing of the water was repeated, still the same extrication of air took place; and "though I repeated," says Dr Priestley, "this process ten or a dozen times with the same water, always letting out the air that was procured by freezing, presently after it was extricated, and before it could have been re-absorbed, yet on exposing it to another freezing I never failed to get more air; and the harder the frost was, the more air I procured." This air he collected, by connecting with a cylindrical vessel of iron, seven or eight inches in height, and near three inches wide at the bottom, a glass tube, the diameter of which was about the fifth of an inch. The apparatus contained about three ounces of water, and it had been made as free as possible from air by previous freezing. The freezing was repeated nine times without changing the water, "and the last portion of air procured in this manner was as great as any of the preceding; so that there remained no reasonable doubt but that air might be procured from the same water in this manner *ad libitum*; and having got near two inches of air in the glass tube, I put an end to the experiment; and examining the air, I found it to be wholly phlogisticated (nitrogen), not being affected by nitrous air, and having nothing inflammable in it *."

From these and his preceding experiments on the production of air, when water passes into vapour, Dr Priestley concluded, that water is convertible into nitrogen gas; he farther supposed a relation to exist between nitrogen and hydrogen, in consequence of which the latter may be converted into the former; and the whole series of facts he considered as favourable to the hypothesis of water being the basis or ponderable part of every kind of air, "the difference between them depending on the addition of some principles which we are not able to ascertain by weight."

It is a curious example of the revolutions of chemical science, that these opinions which were regarded as extravagant, and to which little attention was paid, should be revived, and that they should now appear as the most probable conclusions to which the progress of discovery has led. Mr Davy has presented one or other of them, either that of Girtanner, that nitrogen is a compound of oxygen and hydrogen, or that of Priestley, that water is a simple body, and the only ponderable base of these aëriform fluids, as that suggested by his experiments on the changes produced by galvanism, or by the action of the new substances which these have discovered. In these experiments, particularly in the action of potassium on ammonia, it is stated, that nitrogen disappears, and can be regenerated. " When it disappears, nothing is obtained in its place but oxygen and hydrogen; and when it is formed, its elementary matter is furnished by water. There seem to be at present only two modes of explaining these phenomena, either that nitrogen is a compound of hydrogen and oxygen, or, which is more probable, that hydrogen, nitrogen, ammonia, water, and the nitrous compounds, all contain the same *ponderable* elementary matter, and that their different forms depend upon different electrical states [*]." In the present state of the investigation, it would be useless to speculate further on these singular results.

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* Nicholson's Journal, 4to, vol. iv. p. 193.

CHAP. III.

OF ATMOSPHERIC AIR.

THE elementary nature of atmospheric air, a dogma handed down from the ancient philosophy, was universally admitted by the chemists. Mayow had indeed called this in question; but his conjectures, not thoroughly established, and not well understood, were never regarded. To Scheele the honour is due of having discovered its composition, or of having both observed the facts by which this is established, and drawn from them the just conclusion. This discovery appears to have been made in 1775; Bergman, in his preface to Scheele's treatise, in which it was published, and which is dated 1777, mentioning that it had been written two years before. Lavoisier claims the same discovery. He obviously had views, more or less clear, of the composition of the atmosphere, suggested by the experiments which he performed in 1774 and 1775 *; and in memoirs which he presented to the Academy of Sciences in 1776 and 1777, it is distinctly announced †. Having described the properties of the two gases which compose atmospheric air, we are prepared to enter on its chemical history.

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[*] Philosophical Magazine, vol. xxxiii. p. 173.

The first experiment which Scheele made, and which led to the discovery of the constitution of the atmosphere, consisted in putting 4 ounces of the solution of sulphuret of potassa in a bottle of the capacity of 24 ounce measures, closing the bottle accurately, and inverting it in water, and allowing it to remain in this situation for two weeks, 20 ounce measures of atmospheric air being thus exposed to the action of the liquor. At the end of this period, the cork of the bottle was withdrawn under water, a portion of which immediately rushed into the bottle, shewing that a diminution in the volume of the air had been effected; and this by measurement was found to a-

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* Physical Essays, p. 297. 346. Mémoires de l'Acad. de Sciences, 1775, p. 525.

† Mémoires de l'Acad. des Sciences, 1777, p. 69. 195.

mount to six parts in the twenty *. Various other substances he found to produce a similar diminution, as did also the burning of some inflammables; and on examining the residual air, he found it to be changed in its qualities, —to be lighter than atmospheric air, and to be incapable of supporting combustion †.

How are these phenomena to be explained? Scheele was enabled to give the just explanation, by his previous discovery of oxygen gas. Having observed its property of supporting combustion in a degree so superior to atmospheric air, and finding, that, in the preceding experiments, the atmospheric air was diminished in volume, shewing an abstraction of part of it, and that by this it had lost its power of supporting burning, he concluded, that the portion which had been abstracted was oxygen gas, or what he named Fire Air; and that atmospheric air is a compound of it, and of the air remaining in these experiments, which, it is scarcely necessary to add, is nitrogen gas ‡. The discovery he confirmed, by shewing that pure oxygen gas is totally absorbed by the substances which, in his first experiments, diminished the volume of the air, and that a mixture of it with nitrogen gas is affected in the same way as atmospheric air.

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* This diminution is greater than could have arisen from the mere abstraction of oxygen; and there is reason to believe, from the observations of Dr Austin, that, from the long exposure of the air to the solution, part of its nitrogen had been abstracted, and combining with hydrogen from the solution, had formed ammonia.

† Scheele on Air and Fire, p. 7, &c.

‡ Ibid. p. 35.

Lavoisier inferred the composition of the atmosphere from experiments, in which he observed, that its volume was diminished, and its qualities changed : such were the calcination of metals, the burning of phosphorus, and other inflammables, and the action of nitrous gas. Having likewise made the discovery of oxygen gas, and observed its property of supporting combustion, he concluded, that the diminution of volume in these experiments, and the change of qualities, is owing to its abstraction, and that " the air of the atmosphere is composed of about one-fourth of this gas, with three-fourths of an air mephitic and noxious, and of a nature unknown *.

He afterwards performed an experiment in which the composition of atmospheric air appeared to be clearly demonstrated. It consisted in exposing quicksilver to a heat nearly equal to its boiling point, in a glass matrass, with a bent neck connected with a receiver placed in quicksilver, and containing atmospheric air. A red powder formed slowly on the surface of the quicksilver, the air also diminished in volume; at the commencement of the experiment the quantity contained in the matrass and receiver was about 50 cubic inches; at the end of it, it was found reduced to between 42 and 43. Its qualities were also changed, and it was found, in particular, to be no longer capable of supporting combustion or animal life. The quantity of red matter which had been formed on the surface of the quicksilver was removed ; it amounted to 45 grains; on exposing it to a red heat in a small retort, it returned to the state of running quicksilver, which weigh-

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* Mémoires de l'Acad. des Sciences, 1777, p. 69.

ed 41½ grains, and between 7 or 8 cubical inches of air were collected, which were found to be oxygen gas. On repeating the experiment, so as to collect these airs without any loss, on adding the oxygen gas obtained from the decomposition of the red matter, to the residual air of the first stage of the experiment, an air was formed similar in its properties to atmospheric air.

This experiment is an example both of the analysis and synthesis of the atmosphere. Quicksilver heated in atmospheric air to nearly its boiling point, attracts oxygen; the red substance which forms on its surface is the product of this combination, and the residual air is nitrogen gas. At a higher temperature,—that of a red heat, this compound is again decomposed, the repulsive agency of the caloric overcoming the affinity; the oxygen is expelled, and assumes the gaseous form; and on adding the quantity of gas thus produced, to the residual nitrogen, atmospheric air is reproduced.

The measurement of the quantity of oxygen contained in atmospheric air, or indeed in any gas in which it is not intimately combined, is named Eudiometry, and the instrument by which it is performed, the Eudiometer. To attain such a measurement, it is merely necessary to present to atmospheric air, some substance which combines with its oxygen, and which either does not afford any gaseous product, or affords one that is easily abstracted and measured. Different substances have been applied to this purpose. The fluid originally employed by Scheele, in the analysis of the air,—the solution of sulphuret of potassa, or, what is rather more convenient, the sulphuret of lime, is perhaps superior in accuracy to any, at least if the air be not too long exposed to it, and be not in too small quantity proportioned to the quantity of fluid. Phosphorus is applied by a very simple apparatus; but by its solubility in nitrogen gas, it adds to the bulk of the residual air, for which a correction must be made. Nitrous gas was employed by Priestley; it exhibits the result immediately, but is liable to several sources of fallacy. And hydrogen gas exploded by the electric spark, with a given volume of atmospheric air, likewise gives an immediate result. The application of these substances to this purpose will be more fully stated under the history of each.

From the practice of Eudiometry it was at one time expected, as the name implies, that we should be able to ascertain the purity of air, with regard to its salutary or noxious power on life. It was soon found, however, particularly by Priestley, (and the fact has since also been established by De Marti), that the air of places the most offensive and unhealthy, afforded as much oxygen as that of others of an opposite description: the air, for example, of crowded cities, of low damp situations, or of crowded manufactories, has not been found less pure than that of the country; the noxious quality of the air depending, not so much on any deficiency of oxygen, as on the presence of effluvia not discoverable by this test.

The proportions of oxygen and nitrogen gases in atmospheric air have been variously estimated, from the inaccuracies of eudiometrical processes. Scheele, from his experiments, supposed the quantity of oxygen to be more than 27 parts in the 100; and Lavoisier fixed the proportions at 27, by weight of oxygen, and 73 of nitrogen. Sennebier stated the quantity of it to be 25. Priestley supposed it to vary from 20 to 25. Mr Cavendish supposed it to vary little, and to be not more than 20 in 100: and more lately Humboldt affirmed that it varies from 23 to 28.

There can now be no doubt, that the higher proportions of oxygen are erroneous, and have arisen from inaccuracies in the eudiometrical method from which they were assigned. By phosphorus, the diminution of volume in atmospheric air cannot be carried beyond 20 in 100 parts; by solutions of sulphate or muriate of iron impregnated with nitrous gas beyond 21; by detonation with hydrogen gas it is 21; and by a solution of sulphuret of potassa, which has been agitated with a little atmospheric air, to afford it a small portion of nitrogen, to which it seems to have an attraction, and which, after this precaution, is liable to no fallacy, the diminution, as De Marti found by numerous experiments, is not greater than 22, or rather 21.5 by measure. If it be supposed, what is not improbable, that a little nitrogen is absorbed by the liquor, the proportion will be 21 by measure, or 23 by weight, leaving a residuum which is nearly pure nitrogen, of 79 by measure, or 77 by weight; and this corresponds with the results of the other eudiometrical methods, as established by the experiments of Davy, Dalton, and Humboldt and Gay Lussac. Or, if we take the medium results of the methods that have been employed, the proportion of oxygen will be 21.5.

It was at one time imagined, that the composition of atmospheric air is not uniform, but that it varies both at different parts of the earth's surface, and still more at different heights. Ingenhouz made a number of experiments to prove the former fact, from which he concluded, that the air is purer, or contains more oxygen at sea than on land, and that in the neighbourhood of marshy situations it contains less oxygen than the standard *. Saussure made some experiments on the air at some of the most elevated parts of the Alps, the summit of the Great St Bernard, the Buet, &c.; in this air, the proportion of oxygen was less than in the air on the plains †. Von Humboldt relates, also, that air brought from a great height in the atmosphere, by a person who had ascended in a baloon, contained in 100 parts 25.9 of oxygen, while air at the surface contained 27.6; and that at the summit of the Peak of Teneriffe, the proportion of oxygen amounted only to 19, while at the foot of the mountain it was 27. The proportions which he states proves sufficiently the error of the eudiometrical method he employed, and the eudiometer he did use,—that with nitrous gas, corrected by trying its purity with sulphate of iron,—is indeed the one which is most liable to fallacy. The analysis of the air in the upper regions of the atmosphere, has since been executed with accuracy by Gay Lussac assisted by Thenard. A glass baloon was filled with air at the height of 21,735 feet from the surface, the greatest which has yet been reached, and when opened under water by Gay Lussac after his descent, one-half of its capacity was filled by the water,—a sufficient proof that it had been accurately closed. The air was subjected to trial, both by Volta's eudiometer, and by the solution of sulphuret of potassa;

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* Philosophical Transactions, vol. lxx. p. 354.

† Voyages, t. ii, p. 357.; t. iv. p. 451.

it afforded by the former method 21.49 of oxygen in 100; by the latter 21.63. Atmospheric air at the surface, analysed at the same time in the eudiometer of Volta, gave precisely the same result, 21.49 *. Saussure *junior* also found, that the air on the summit of the Col-du-Geant contained within one-hundredth part as much oxygen as that on the plain, and even this difference may be ascribed to the difficulty of making the experiment with perfect accuracy. The uniformity of the composition of the atmosphere at different parts of the earth's surface, appears also to be established. Mr Cavendish originally observed, that air subjected to examination at different times, and air likewise from different places, was of perfectly similar composition †; and the same observation had been made by Fontana from his own experiments ‡. Mr Davy states, that no sensible difference was found in the air sent from the coast of Guinea and the air in England §. Berthollet found, that the air in Egypt and in France was similar, affording 22 of oxygen in the 100, any difference observed amounting not to a two hundredth part of the air submitted to trial ||. De Marti, by experiments in Spain, obtained the same uniformity of composition (between 21 and 20 of oxygen in the hundred parts) in the air at places at a distance from each other; and he adds also, as established by his experiments, that in every state of the atmosphere, whether with regard to temperature, to pressure

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* Nicholson's Journal, vol. x. p. 286.

† Philosophical Transactions, vol. lxxiii. p. 129.

‡ Ibid. vol. lxix.

§ Journals of the Royal Institution. vol. i. p. 48.

|| Memoirs relative to Egypt, p. 326.

as indicated by the barometer, to winds, to humidity, to the season of the year, or the hour of the day or night, the results were precisely the same *. And the researches of Humboldt and Gay Lussac, made with the view of determining this question, have established the same conclusion †.

In the constitution of the atmosphere, we perceive a striking singularity. Its ingredients, though of different specific gravities, do not separate, and it is every where of uniform composition,—a fact which appears to lead to the conclusion, that its principles are chemically combined. But, on the other hand, it has no qualities different from those of its constituent parts, nor do these appear to be altered, farther than by mere dilution. In presenting them, too, to each other, they mix equally well, and remain permanently diffused through each other, in every proportion, and no change of temperature can be observed to indicate any intimate chemical action. Yet under other circumstances, these gases obey the usual laws of chemical attraction, enter into intimate union, and form compounds endowed with very peculiar properties.

On either hand, therefore, there appears a difficulty. If their particles are retained by no mutual attraction, why do they not separate, from the difference in their specific gravities? If they are united by any attraction, why is this not marked by the usual consequences of chemical union, a change of temperature at the time it happens, and a change of properties?

This difficulty has frequently engaged the attention of

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* Journal de Physique, t. lii. p. 173. † Id. t. lx. p. 152.

chemists, and some have been disposed to regard the union between the gases, composing the atmosphere, as of a chemical nature; others as merely mechanical, without giving any very satisfactory explanation of the facts that appeared adverse to either opinion. Mr Dalton at length proposed a theory of the constitution of the atmosphere, on the principle that it is a mechanical mixture, which accounts for the fact apparently irreconcilable with that hypothesis, the gases remaining uniformly mixed, and which is undoubtedly entitled to the praise of great ingenuity.

Mr Dalton's hypothesis rests on two assumptions: 1st, That the particles of any individual gas repel each other, a fact of which there can be no doubt. 2dly, That the particles of mixed gases neither attract nor repel each other, but are perfectly indifferent, and not affected by their mutual proximity. From these it follows, that if two gaseous fluids are mixed together, though of different specific gravities, they will soon be diffused, and intimately mixed, and will remain so without any tendency, under the circumstances in which they exist, either to separate or to unite. Each gas, from its own elasticity, or the repulsion between its particles, diffuses itself over the space in which they are confined: by the hypothesis, its particles exert no attraction to those of the other, hence there can be no union; by the same hypothesis, they do not repel those of the other, hence there is no cause to alter the arrangement which each would assume, or every gas is as vacuum to every other. It is scarcely necessary to point out the application of these assumptions to the explanation of the constitution of the atmosphere. Suppose that on any part of the earth's surface there rests a column of oxygen gas; this, from its elasticity, will rise to an indefinite height, becoming less dense as it recedes from the surface, as being subjected to less pressure. If, on the same surface, a column of nitrogen gas be supposed to rest, its particles will equally recede, and will be intimately mixed with those of the oxygen; other gases, carbonic acid for example, or watery vapour, may be thrown in, and will be arranged in the same manner; and thus, on the same surface, will rest so many columns of gases, each intimately blended, indifferent to the other, supported by its own elasticity, and the inferior strata of each pressed only by its own incumbent particles. Such may be the atmosphere surrounding the earth, at least on such an hypothesis may be explained the apparently discordant facts, that the gases composing it do not separate, but remain uniformly mixed, while, at the same time, they shew no marks of having entered into chemical union. It is even contended by Mr Dalton, that such must be its constitution, or that the principles he assumes must be just, and that an absurdity is involved in any other. Only one of three suppositions can be admitted,—that the particles of mixed gases attract each other,—that they repel each other,—that they neither attract nor repel: were the first true, these particles, Mr Dalton conceives, must be brought into union, which of course would be discovered by the usual consequences of chemical combination; were the second just, they must separate if of different specific gravities, even where they had previously been intimately mixed, and the heavier fall to the under part of the space they occupy. Neither of these is the case with regard to the airs composing the atmosphere, and hence he conceives must follow the third principle, on which his hypothesis rests *.

Notwithstanding the apparent strictness of this reasoning, more is perhaps involved in it than what necessarily follows, and a view of the constitution of the atmosphere may be delivered, in conformity to the principle, that the gases of which it consists exert a mutual attraction. One of this kind I have been accustomed to illustrate in my Lectures, and I stated briefly its principle in the following sentence in an early publication. "Perhaps that chemical attraction which subsists between the solid bases of these gases, but which, when they are merely mixed together, cannot, from the distance at which their particles are placed by the repulsive power of caloric, bring them into intimate union, may still be so far exerted, as to prevent their separation: or, they may be retained in mixture by that force of adhesion, which, exerted at the surfaces of many bodies, retains them in contact with considerable force †." This principle, that chemical affinity may be exerted between the particles of mixed gases, so as to prevent their separation, but not with such force as to bring them into intimate combination, is in itself sufficiently probable, and it affords an explanation of the phenomena connected with the constitution of the atmosphere. The particles of oxygen and nitrogen gases, its chief constituents, have a mutual affinity, for they can be intimately combined together. At the temperature at which they exist in

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* Manchester Memoirs, vol. v. Part II.

† Elements of Chemistry, vol. i. p. 207.

the atmosphere, this is not sufficient to overcome their elasticity, and unite them so as to detach their caloric, and form a new substance. But it may not be entirely dormant, but may be so far exerted, as to keep them in a state of adhesion, or prevent their separation, or even produce a degree of approximation, so inconsiderable, however, as not to be discovered by any considerable change of volume, (and that a slight increase of density does follow the mixture of oxygen and nitrogen gases, has appeared to be the fact to several chemists, though, if it be inconsiderable, it is obvious that it must be difficult to discover it with accuracy). This hypothesis derives additional probability from the views of chemical affinity, which have been presented by Berthollet ; and his theory of the chemical nature of the atmosphere is precisely that which I have now stated. I consider it as preferable to Mr Dalton's. The discussion by which I would endeavour to establish that preference, will be better placed in a note. Note D.

I have hitherto spoken of atmospheric air, as if it were composed only of oxygen and nitrogen gases. Another gas, carbonic acid,—the Fixed Air of the old nomenclature, is always found in it. It is discovered by exposing to the atmosphere substances which have a strong attraction to this gas, and which combine with it at natural temperatures. If lime-water, for example, be exposed, the lime dissolved in the water attracts the carbonic acid in the atmosphere, and forms a compound, which being insoluble in water, appears as a pellicle on the surface, and augmenting, at length breaks and falls to the bottom. The quantity is inconsiderable, and is not easily ascertained with accuracy. That it is inconsiderable, is evident, since tincture of turnsol, which is reddened by this gas, receives no tinge when a small quantity, a cubic inch, for example, is agitated for a long time with a large quantity, 700 or 800 cubic inches of atmospheric air, as Fontana long ago remarked. It used to be estimated at 1 in 100; but this is a proportion undoubtedly too large. Mr Dalton, from an experiment, supposes it not to exceed 1 in 1000. He finds, that if a glass vessel filled with 102.400 grains of rain-water, be emptied in the open air, and 125 grains of strong lime-water be poured in, the mouth closed, and the vessel agitated, this portion of lime-water is saturated by the carbonic acid in this quantity of atmospheric air. But 125 grains of the lime-water used, he found, required for saturation 70 grain measures of carbonic acid gas; this quantity of carbonic acid, therefore, it may be inferred, is contained in 102.400 grain measures of atmospheric air, or the proportion by measure is $\frac{1}{1400}$th of the whole, which, from the relative specific gravities of carbonic acid gas, and atmospheric air, is by weight very nearly $\frac{1}{1000}$th [*].

As carbonic acid is produced by the respiration of animals, by combustion, and other processes at the surface of the earth, it has been supposed that the quantity of it found in the atmosphere is derived from these sources, and that it exists only near the surface. Such, no doubt, may be, and probably is its origin. At the same time, from the reciprocal attraction which gases exert, it is uniformly diffused; its proportion, so far as it can be ascertained, is nearly the same; and though of greater specific gravity than the other gases in the atmosphere, it is found at the greatest heights, and at a distance from any immediate source of this kind, Saussure having found it in the air at the summit of Mont Blanc *; and Von Humboldt, in air brought down from a great height in the atmosphere by means of a balloon †. Mr Dalton found that the air in an assembly, in which two hundred people had breathed for two hours with the windows and doors shut, contained little more than 1 of carbonic acid in 100.

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[*] Manchester Memoirs, new series, vol. i. p. 254.

A portion, too, of watery vapour always exists in the atmosphere, evidently derived from the evaporation of water at the surface, and varying in its quantity according to temperature, and other circumstances not well ascertained. The quantity at any given temperature and pressure, it is not easy to determine with accuracy. The maximum has been fixed by Saussure at 10 or 11 grains of water in a cubic foot of air at the temperature of 65°, and under a medium pressure ‡; others have stated it higher. Mr Dalton, without determining the greatest quantity, observes, that the portion of watery vapour in the atmosphere varies considerably, principally according to temperature. In the torrid zone it is capable of exerting a pressure on the surface of the earth equal to from 0.6 to one inch of mercury; in our climate it rarely amounts to a pressure of 0.6, and in winter is sometimes so low as 0.1. From assumptions, which perhaps are hypothetical, he supposes

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* Voyages dans les Alpes, tom. vii. p. 323.

† Philosophical Magazine, vol. i. p. 333.

‡ Essais sur l'Hygrometrie, p. 141. 185

that at the temperature of 55°, the force of vapour in the atmosphere at an average is equal to .443 of mercury, or nearly $\frac{1}{70}$th of the whole atmosphere *.

While the water in the atmosphere preserves the aërial form, the air containing it is perfectly transparent; even in this state, however, it can be discovered existing in it, by substances which have a strong affinity for water, imbibing it when exposed to such an atmosphere. Thus lime exposed to the driest air soon slakes, an operation owing to its combination with water. When the vapour is condensing, it communicates to the atmosphere a degree of opacity from the conglomeration of particles of water. This, according to the extent to which it happens, gives rise to the natural appearances of clouds, mist, and rain.

Spontaneous Evaporation, as the natural process by which water is elevated in vapour in the atmosphere is termed, is promoted by various causes. It takes place with more rapidity as the temperature is high; hence it is greatest in warm climates; it is favoured by a dry atmosphere, and still more by agitation and quick removal of the air; hence the drying effect of winds. By this addition of watery vapour to the atmosphere, its elasticity is augmented, it becomes lighter, and the portion of air receiving it therefore ascends †.

Different theories have been proposed, to account for the elevation of water in vapour, and its suspension in the atmosphere at natural temperatures. According to the

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* Manchester Memoirs, new series, vol. i. p. 253.

† Philosophical Transactions, vol. lv. p. 146.

theory of Halley, afterwards very clearly illustrated by Hamilton *, this is owing to a chemical affinity subsisting between air and water, so that evaporation is similar to solution, to which it was accordingly compared. According to Saussure, the water is converted into vapour by the agency of caloric, but the vapour thus formed he supposed to exist in the atmosphere, combined with its constituent gases; and lastly, according to De Luc, and likewise according to Mr Dalton's views, water is elevated in vapour solely by the agency of caloric, and exists in the atmosphere in a state of mechanical mixture or diffusion. The discussion of this question being connected with the theory of the constitution of the atmosphere, I shall refer it to the same note. Note D.

Spontaneous evaporation is of much importance in the economy of nature, as the great process by which water is distributed over the surface of the globe, and its perpetual circulation established.

The atmosphere consists, then, of oxygen, nitrogen, carbonic acid, and aqueous vapour, and the proportions will be nearly as follow:

Nitrogen gas,	77.5 by measure,	75.55 by weight.
Oxygen gas,	21 ———	23.32
Aqueous vapour,	1.42 ———	1.03
Carbonic acid gas,	.08 ———	.10

It has been imagined that a portion of hydrogen may exist in atmospheric air. In the usual analysis of it, oxygen is abstracted, and the residual air is found to be nitrogen. But there is no experiment by which it is pro-

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* Philosophical Transactions, vol. lv. p. 146.

ved that this nitrogen is perfectly pure; on the contrary, it is possible that a portion of hydrogen may be mingled with it, which, from the quantity not being considerable, may not be easily detected. If even hydrogen be added to atmospheric air, in the proportion of 6 in 100, it has been found by Humboldt and Gay Lussac that the mixture is not inflamed by the electric spark. They have proved, however, at the same time, that no sensible portion of hydrogen is contained in atmospheric air, as, when a comparative analysis was made of common air, and of an artificial air, composed of 20 of oxygen and 80 of nitrogen, each perfectly pure, by detonation with a measured quantity of hydrogen, the results were in both precisely the same *.

Many other substances must be present in atmospheric air, though in quantities too minute to be detected by chemical analysis. Not only do a number of bodies pass into vapour at the surface of the earth from the effect of temperature; but the air, by its action, promotes this vaporization, and under exposure to it bodies pass freely into vapour, which, at the same temperature in vessels having an imperfect communication with the air, do not evaporate. This important fact has been very well established by Gay Lussac †.

The properties of atmospheric air appear to be merely the aggregated properties of the gases of which it consists. It is invisible, inodorous, insipid, compressible, permanently elastic. Its specific gravity is .0012279, the medium,

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* Journal de Physique, tom. lx. p. 158.

† Mémoires de la Société d'Arcueil, p. 204.

as nearly perhaps as can be estimated, of the specific gravities of the oxygen and nitrogen gases, in the proportions in which they are mixed. 100 cubic inches weigh 31 grains. It supports combustion; and as it does so from the oxygen it contains, the combustion is less rapid and vivid, and continues for a shorter time than in oxygen gas. By the same agency it supports animal life; a portion of its oxygen is consumed in respiration; it has also been supposed that there is a consumption, though to a less extent, of its nitrogen; but this, it now appears, is not the case. It is very sparingly absorbed by water. The absorption, too, is unequal, more of the oxygen being combined with the water than of the nitrogen. Schèele observed, that when agitated with water, the oxygen was absorbed in preference to the nitrogen; by using boiled water, and agitating a small portion of air with a large quantity of water, and keeping them in contact for a number of days, so much of the oxygen was absorbed, that the residual air extinguished a burning candle. It is difficult, even by long boiling, to expel from water the whole of the oxygen which it holds dissolved; and, if exposed again to the atmosphere, it very quickly imbibes it. Water freed from this air, which it holds loosely dissolved, is tasteless and vapid *.

Atmospheric air is an important agent in many of the operations of nature. Besides serving as the vehicle of the distribution of water, it is, by its mobility, the principal agent by which temperature is in some measure equalized, or at least its extremes moderated. Animals are im-

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* Treatise on Air and Fire, p. 164.

mediately dependent on it for life. It is supplied by respiration; in the more perfect animals, its deprivation cannot be sustained for a few minutes; and even in the less perfect, the abstraction of it is followed, though not so immediately, by death. Its agency depends principally on its oxygen, a quantity of which is spent in every inspiration, in producing chemical changes in the blood. Vegetable life is also in some measure dependent on it; it conveys water, and perhaps also carbonic acid, and even other principles, to the leaves of plants, and is thus subservient to their nutrition and growth.

An interesting subject in the history of the chemical constitution of the atmosphere, is the consideration of the means by which that uniformity, in its composition, which is adapted to so many important purposes, is preserved. By the operations constantly carrying on at the surface of the earth, respiration, combustion, and the decomposition of animal and vegetable matter, it is suffering constant changes; its oxygen is consumed, and carbonic acid and various other gases are disengaged and communicated to it. How are these changes regulated, so as to preserve the atmosphere in its proper purity?

Dr. Priestley, in consequence of his experiments on the means of restoring the purity of atmospheric air, pointed out vegetation as the important natural process by which this is chiefly effected. From these experiments, supported also by those of Ingenhouz, it appeared, that growing vegetables, exposed to the solar light, emit oxygen from their leaves; and it was afterwards proved, that they absorb carbonic acid by the under surface of the leaf as well as by their roots, which appears to be decomposed in their vessels, and to serve for the formation of their products. Hence was suggested an admirable view of the mutual adaptation of the animal and vegetable kingdoms; the individuals belonging to the one, consuming oxygen and expiring carbonic acid; those of the other absorbing carbonic acid, and restoring oxygen to the atmosphere. Such a view is conformable to the general economy of nature, but there is much reason to doubt if the supposed facts on which it rests are sufficiently established. The subject is involved in obscurity, and it is not improbable that there are other natural processes by which the balance is adjusted, and the constitution of the atmosphere so uniformly preserved. If the relation, which late discoveries point out, between oxygen, nitrogen, and water, be established, this will probably be illustrated.

CHAP. IV.

OF THE CHEMICAL AGENCY OF OXYGEN IN ITS PURE FORM, AND AS IT EXISTS IN ATMOSPHERIC AIR.

THE general chemical agency of oxygen, it has been remarked, is more important than that of any other principle; its affinities being more extensive, and apparently more energetic. These affinities, and the actions which result from them, are exerted by it not only in its pure form, but likewise as it exists in atmospheric air, and this with nearly the same force, and with similar results. It is even more generally as a constituent part of atmospheric air that it operates as a chemical agent. I have therefore reserved the general view of its chemical action until the constitution of atmospheric air has been explained. This view I have now to deliver.

The combination of oxygen with other bodies is often attended with the extrication of light, and the production of heat, giving rise to the phenomena of combustion. The illustration, therefore, of this important chemical process, belongs to the statement of the general agency of oxygen.

The phenomena of combustion, and the distinction of bodies into Combustible or Inflammable, and Incombustible or Uninflammable, are sufficiently familiar. The latter, when exposed to heat, have their temperature raised, and that in proportion to the degree of heat applied to them; but whenever this communication of caloric from an external source is stopt, their temperature falls, and they return to their former state. Combustible bodies, on the contrary, when heated to a certain point, begin to suffer a very evident change; they become much hotter than the surrounding bodies, emit light more or less copiously, and appear to be consumed, or, to speak more correctly, are converted into substances altogether new, and which frequently are not apparent to the senses. It is this rapid emission of light and caloric, and this change of properties, and apparent loss of substance, which constitute the process usually termed Combustion.

Although the phenomena of combustion are so striking, no rational theory was proposed to account for them until Beccher advanced his hypothesis. He supposed that there existed in all combustible bodies a peculiar kind of matter, which he named inflammable earth, and that this matter, put in motion, exhibited the phenomena of heat and light. Such bodies only are combustible, according to this opinion, as contain this inflammable earth.

Stahl extended and refined this hypothesis. With Becher he attributed the inflammability of bodies to their containing a common principle. This principle, however, he did not conceive to be of an earthy or solid nature, nor did he suppose fire to be the effect of any peculiar motion. The inflammable principle he considered as one more subtle, as being merely the matter of heat and light, pure fire, or, as he named it, Phlogiston. Combustion, therefore, is merely the disengagement of this principle: Inflammable substances are compounds of it with certain bases; and, when it is expelled, their inflammability is lost, and a substance is left possessed of very different properties. Phlogiston is likewise supposed to be capable of being transferred from one body to another, without being rendered sensible by the appearance of heat or light; and by this transfer, the body which is deprived of it, suffers a change similar to that produced during combustion, while that which receives it acquires of course the property of inflammability.

In the original hypothesis, as Lavoisier has justly observed, there is little merit. It required no great effort to say, that inflammable bodies burn because they contain an inflammable principle; but it involves a general fact, for the discovery of which we are indebted to Stahl, and which is an important truth, that the property of inflammability may be lost by a body, and restored to it by the agency of another, which loses it in its turn.

The hypothesis of Stahl being capable of being applied to a number of chemical phenomena, so as apparently to afford a satisfactory solution of them, was universally adopted, nor for a considerable period was any doubt entertained of its truth.

As it was a mere hypothesis, however, founded on an imperfect knowledge of the phenomena which it was designed to explain, its imperfections gradually became apparent. Stahl had overlooked the influence of the air in combustion, though even before his time it had been demonstrated by Mayow and Boyle. Of the necessity of its presence to support this process, the phlogistic doctrine gave no account. It had likewise been observed, and even ascertained by experiment, that though in some cases the combustible body appears to be consumed during combustion, in others it increases in weight, and that to a considerable amount,—a fact inexplicable on the Stahlian hypothesis, since the disengagement of phlogiston, from the inflammable body, ought rather to diminish its gravity, or, if it were too subtle to produce this effect, still no cause could be pointed out why the weight should be increased. This increase of weight had even been ascribed by Hales to the air which is absorbed; but this explanation seems to have been little attended to, and various attempts were made to solve these difficulties, in conformity to the doctrine of a phlogistic or inflammable principle, though with no great success.

At this time the experiments of Black, Priestley, Cavendish, and others, directed the attention of chemists more particularly to the influence of the air in combustion; and, in consequence of the facts which were discovered, various modifications of the doctrine of Stahl began to be proposed, in which more or less deference was paid to the principles of the original theory. Bayen and Lavoisier were the first chemists who doubted of the truth of the theory itself, so far at least as to explain some of the phenomena usually referred to it, on a different principle. Bayen having been occupied with experiments on some of the metallic precipitates in which he had observed the increase of weight, with the view of ascertaining if this was owing to air combined with the metal, endeavoured to discover, if, in reducing them to the metallic state, any air was given out. After various experiments, in which they were reduced by heating them with charcoal, and in which a large quantity of air was obtained, he succeeded in reducing some of these precipitates by heat alone, and observed, that, during the reduction, a large quantity of elastic fluid was given out, which he collected over water. From these results he concluded, that " the language of " the followers of Stahl could be no longer held, and that " they will be forced to restrict their doctrine with regard " to phlogiston,—either to admit that these mercurial pre- " cipitates are not metallic calces, although some of their " most celebrated chemists have considered them as such; " or that there are calces which may be reduced without " the agency of phlogiston *." And again, these " experiments lead me to conclude, that in the mercurial calces, the mercury has its calcined state, not from the loss of phlogiston, but from its intimate combination with the elastic fluid, of which the weight added to that of the

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* Opuscules Chimiques, tom. i. p. 263. 282.

mercury, is one of the causes of the increase of weight which I observed in the precipitates submitted to examination[*].

Lavoisier has been said to have derived his system from these ideas of Bayen; but the charge is unjust: some of his researches on the same subject were prior, and are even referred to by Bayen, in his first memoir on the mercurial precipitates[†]. Lavoisier had been occupied about the same time with similar researches, and had formed similar views, which he gradually extended and matured into a complete system. He established (what had before been observed by Boyle and Hales, though the observation had not been much attended to,) that in combustion, and the analogous process of metallic calcination, the air is diminished in volume, and that this diminution stops at a certain point. He proved, too, by experiment, what had likewise been previously known, that the substances subjected to such processes increase in weight; and he observed, that in the reduction of metals, a quantity of air is given out. These experiments were given in a work published in 1774[‡]. Even then they suggested to him, "that the air of the atmosphere, or an elastic fluid con-
" tained in the air, was capable, in many instances, of be-
" ing fixed and combined with metals; that to the addi-
" tion of this substance, the phenomena of calcination are
" owing, and perhaps several other phenomena, of which
" philosophers have as yet given no satisfactory explana-

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[*] Opuscules Chimiques, tom. i. p. 228. 258.

[†] Journal de Physique, 1774.

[‡] Physical and Chemical Essays.

"tion [*]." He extended the same conclusion to combustion, and observed, as the consequence necessarily following, that if it were just, the combustible body should be incapable of burning *in vacuo*, which, on making the experiment with sulphur and with phosphorus, he found to be the fact. In subsequent experiments, published in the Memoirs of the Academy of Sciences, he added to the evidence of these conclusions; he shewed more clearly that it is the oxygen of the atmospheric air that is absorbed in combustion; that it adds to the weight of the combustible body, this increase being equal to the weight of the oxygen that disappears; that it may be recovered from it either in a pure or combined state; that the result of this process is frequently the production of an acid; and that oxygen may be regarded as the principle of acidity [†].

Dr Black had, long prior to these discoveries, established the important truth, that in vaporisation there is an absorption of caloric, which becomes latent; that when a gas is formed, a quantity of caloric is absorbed by it, without producing augmentation of temperature; and that, in the condensation of an elastic fluid, caloric is given out. Lavoisier availed himself of these discoveries, perhaps, without sufficient acknowledgment. Considering aëriform fluids as containing a large portion of caloric in a combined state, and having proved that the oxygen of the atmospheric air passes into combination with the combustible body, this combined caloric he supposed to be extricated, and to be the source of the heat and light which attend the process. "The air," says he, "I consider as "a compound of the matter of fire with a substance which "is its base; when a substance is presented to this base, "with which it has a greater affinity, the matter of fire "becomes free, resumes its properties, and appears with "heat, flame, and light *."

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[*] Physical and Chemical Essays, p. 297.

[†] Mémoires de l'Acad. des Sciences, 1775, p. 520. Ibid. 1776, p. 671. Ibid. 1777, p. 65. 195.

The merit of Lavoisier does not consist so much in having established the facts on which his theory rests, for this had in part at least been done by others, and it is difficult to say how far he had derived assistance from their labours: It is better founded on the justness of the conclusions which he deduced from them. It is not easy, after a philosophical system has been subverted, and we have become familiar with the evidence by which its falsity has been demonstrated, to estimate duely the impression which it once made, and the effort which was necessary for its rejection. We may in some measure judge of the possession which the Stahlian doctrine had of the minds of chemists, by the universal assent it had received, and the pertinacity with which the speculations of Lavoisier were for a time rejected. Though the first rank in science cannot be claimed from a generalization, which in some measure resulted from the progress of the department of knowledge to which it belongs, and which after all is imperfect; yet high honour cannot be denied to him who suffered not his mind to be biassed by a prevailing system; who, when the subject engaged the at-

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* Mémoires de l'Acad. des Sciences, 1777, p. 420. 592. 597.

tention of men of the first eminence, perceived the fallacy of what commanded their assent, and, in opposition to their exertions, succeeded in establishing the truth.

Lavoisier indeed was soon aided in France by philosophers of distinguished talents, La Place, Monge, Berthollet, and others ; and for some time the contest between the ancient and modern systems was warmly maintained. The original doctrine of Stahl could indeed be no longer defended, but various attempts were made to reconcile it with the modern discoveries. It could not be denied, that in combustion oxygen gas is consumed ; but instead of admitting the simple conclusion of Lavoisier, that this oxygen combines with the inflammable body, and that the phenomena of combustion are the result of this combination, it was attempted by various hypotheses to maintain the agency of a principle existing in inflammable bodies, and to preserve at least the language of Stahl. There were thus established, as Lavoisier in one of his memoirs remarked, " a number of doctrines, in which nothing of the " original system remained but the name of phlogiston ; " every one attached to this word a vague idea, which no " one rigorously defined ; and they united, without per- " ceiving it, in the same agent the most opposite and in- " compatible properties."

Of these hypotheses it is now unnecessary to take any notice. Scheele's, inferred from his own discoveries, is distinguished by its boldness and ingenuity. He supposed that the oxygen which he proved to be consumed in combustion, combines, not with the combustible body, but with the phlogiston it contains, and forms the heat and light which are evolved,—a supposition which accounted sufficiently indeed for the necessity of oxygen to excite and support combustion, and for its consumption during the process, but which left unexplained the increase of weight which the combustible body gains. Kirwan's was better adapted to the phenomena. He supposed that the oxygen consumed, combines with the phlogiston of the inflammable matter, which he supposed to be, not the principle of fire of Stahl, but the base of inflammable air, or hydrogen; that it forms with it a compound which remains united with that matter, and increases its weight. Previous to the discovery of the composition of water, this hypothesis had some advantages, which were lost when that discovery was made. Less simple than the doctrine of Lavoisier, and supported by no proof, it was at length with much candour relinquished by its author; and since that time the discussion on the theory of Stahl might be regarded as closed. Yet even still it appears to have its influence, and it is a striking trait of prepossession to perceive in the developement of new facts, and in the progress of the science, reference often made to an opinion advanced in its infancy, and which, to give it its highest praise, can be regarded only as an ingenious conjecture.

I have now to state the facts by which the modern doctrine is established. Its first principle is, that combustion is the combination of oxygen with the combustible body. This is proved from the presence of oxygen being indispensable to that process; from this oxygen being consumed; from the increase of weight which the combustible body always gains during combustion corresponding exactly to the weight of the oxygen that disappears; and from this oxygen being again recoverable either in a free or combined ſtate from the ſubſtance remaining when the combuſtion has ceaſed.

1st, Combuſtion cannot go on without the preſence of oxygen, and is more vivid where the oxygen is in a pure unmixed ſtate. This is proved by innumerable experiments. If a burning body be immerſed in nitrogen, hydrogen, or any other gas, which does not contain oxygen, it is immediately extinguiſhed ; or, if placed under a jar on the plate of the air-pump, on exhauſting the air the flame is gradually extinguiſhed, and the combuſtion ceaſes, while, in another jar of the ſame ſize, placed with its orifice in water, ſo as to cut off the communication of the air, it will continue burning for a longer time. Even in this laſt ſituation, however, it will be in a certain time extinguiſhed, that is, after the portion of oxygen contained in the atmoſpheric air in which it is placed is conſumed. If, on the other hand, the combuſtible body be placed in pure oxygen gas, the combuſtion is more vivid, and continues a longer time than in atmoſpheric air.

It is even poſſible, by thus placing combuſtible bodies in oxygen gas, to cauſe thoſe to burn which in atmoſpheric air are not capable of combuſtion, or at leaſt are not capable of it unleſs a great heat be kept up. Iron, for example, if heated red hot, and ſuſpended in atmoſpheric air, does not burn, but ſuffers its temperature to be gradually reduced, but if ſuſpended in oxygen gas, its combuſtion is vivid.

There is only one apparent exception to this propoſition. When an inflammable body is mixed with an equal weight of nitre and kindled, it burns with rapidity, though the atmoſpheric air be excluded. With ſeveral other ſaline substances, the effect is the same. But this is still a confirmation of the general proposition; for these substances contain a large proportion of oxygen which they yield to the combustible body, and by which the combustion proceeds, independent of the presence of air.

2d, In every case of combustion, the oxygen present is consumed. This is proved by the facts, that a combustible body burns in atmospheric air only for a certain time,—that the air is diminished in weight and bulk,—and that the combustion ceases when the diminution of volume amounts to about one-fourth part, that is, when the oxygen has all been absorbed. In pure oxygen gas, the diminution of volume is much greater, and, could the experiment be performed, combustion might be carried on until the whole of the oxygen, if it were pure, would be consumed.

This consumption of oxygen takes place in the burning of every kind of inflammable matter, though there are many cases in which the diminution of volume in the air does not appear considerable. But this is owing to the new substance, produced by the combination of the oxygen with the combustible body, being one which exists in the gaseous form, and of course which remains mixed with the nitrogen of the atmosphere. When this is removed, the diminution is found to be the same as in any other case of combustion.

It is to be observed also, that in combustion in atmospheric air, the process generally ceases before the oxygen is entirely consumed. When the greater part of it has combined with the inflammable body, the remaining portion of it becomes so much diluted with the nitrogen gas, that the combustion languishes, and at length so little oxygen is in contact with the burning body that it stops.

3d, In combustion, the combustible body always increases in weight, and the increase corresponds exactly to the weight of the quantity of oxygen gas which disappears during that process.

This Lavoisier proved by several experiments. He found that phosphorus, in burning, absorbs more than one and a half its weight of oxygen gas, 45 grains of it consuming 69 of oxygen; and that the weight of the substance produced, during the combustion, "exactly equals the sum of the weight of the phosphorus consumed, and oxygen absorbed." He proved the same with regard to sulphur, charcoal and several of the metals. Thus, in the combustion of 100 grains of iron, he found that 70 cubical inches of oxygen gas were consumed, and the iron had increased in weight 35 grains. But a cubic inch of oxygen gas weighs just one-half grain; the weight, therefore, of the 70 inches was 35 grains, corresponding exactly to the augmentation of weight in the iron.

The case is the same whatever combustible body be burnt; and the proposition with respect to combustion may be stated as universal. There are some cases, however, which, to superficial observation, would appear to be exceptions; as in the combustion of wood or coal, where there is only a small quantity of ashes left after burning, not the hundredth part of the weight of the fuel itself. But, in this case, the principal product of the combustion is a substance which assumes the gaseous form, and which therefore escapes unobserved: but if the combustion of such bodies be carried on in vessels adapted to collect all the products, both volatile and fixed, it will be found, that their weight is equal to the sum of the weights of the inflammable body, and of the oxygen consumed.

Lastly, the quantity of oxygen which is absorbed during combustion, may always be recovered from the compound that has been formed; and the weight of this gas is equal to the weight of the quantity which has disappeared during the combustion.

Thus, when mercury is heated in atmospheric air, it attracts its oxygen, and is converted into a red powder. If this powder be exposed to a still stronger heat, it is again decomposed, oxygen is disengaged, and it returns to the state of running mercury. If this oxygen be collected, it will be found that it is precisely equal to the quantity which had been attracted by the mercury from the atmospheric air.

In other cases, the oxygen cannot be expelled from the inflammable body by the operation of heat. But it may be separated by the superior attraction of a third substance; and in this case, the compound formed by the direct union of that substance with oxygen is obtained. Thus iron unites with oxygen, and the compound cannot be decomposed by heat. But if this compound be exposed to heat with a portion of charcoal, this substance exerts a more powerful attraction to the oxygen than the iron does; the iron is reduced to the metallic state, and the compound of charcoal with oxygen,—the substance known by the name of Carbonic Acid, is disengaged. It being ascertained by previous experiments, how much oxygen is contained in a certain quantity of this compound, the quantity of that principle which was combined with the iron, can be determined by the quantity of carbonic acid produced.

By these facts, then, Combustion is proved to be the combination of oxygen with the burning body. Combustibles are substances having an attraction to oxygen ; and the substances formed by the combustion are compounds of oxygen with these bodies.

Like other chemical combinations, this is much influenced by the temperature of the bodies. In general, the combination does not take place but at a high temperature, and therefore the application of heat is necessary to cause the combustion to commence. But after it is begun, it generally continues to go on while the air is freely admitted, as much caloric being extricated by the combustion as is sufficient to keep up the necessary temperature.

This temperature is different in different bodies. In some, as phosphorus, a moderate heat is sufficient ; in others, as sulphur or alkohol, a higher temperature, equal to about 300°, is necessary ; charcoal must be heated to ignition, and the greater number of the metals require to have their temperature raised far beyond this, to enable them to combine with oxygen.

The effect of temperature, in exciting or promoting combustion, is to be explained on the same principles as its effect in accelerating any chemical combination ; its principal operation is that of diminishing the cohesion of the combustible body, which is an obstacle to the attraction exerted between it and the oxygen, though this is also modified by the increase of elasticity at the same time in the oxygen gas.

Having thus established the cause of combustion, it remains to explain from it the phenomena which are exhibited. The principal of these are the disengagement of light, and evolution of caloric.

By the older chemists, it was supposed, that the caloric rendered sensible during this process, proceeds from the inflammable body, and this remains the popular opinion. It is one which must appear unquestionable while the nature of combustion is imperfectly understood. The combustible body appears luminous, and feels intensely hot; no other agent appears to be concerned; it seems, therefore, the unavoidable conclusion, that it is from the combustible body itself that the light and caloric are evolved.

But when the influence of the air in combustion is discovered,—when it is proved, that this process is nothing more than the combination of the combustible matter with one of the constituent parts of the atmosphere, the oxygen gas, it is evident, that the former conclusion no longer necessarily follows; for where two bodies are concerned, if, from their mutual action, light and caloric are evolved, it is *a priori* equally probable, that they may be derived from the one, or the other, or from both. In combustion, these principles, from whatever source they may be derived, must be separated where the oxygen gas and the combustible body are in the act of combination, that is, upon the surface of the burning body, and consequently it will appear luminous, while the gas being invisible, escapes observation. But this affords no proof that it is from the combustible body that they are derived, and it becomes necessary, by a farther examination, to discover whence the evolution of light and caloric proceeds.

The explanation of the production of heat in combustion, is to be derived from the discoveries of Black, Irvine, and Crawford. Dr Black had established the important truth, that bodies existing in the aërial form, contain at the same temperature more caloric than fluids or solids; and that when aëriform fluids are reduced to the fluid or solid state, they render sensible a great portion of the latent caloric they contain. When it was proved, therefore, that in combustion, an aërial body enters into combination, and passes generally into a denser state, it was an obvious conclusion, that from its condensation the heat evolved might be derived. Though approaching to the truth, however, this explanation is not perfectly correct; it is not to the mere condensation of the oxygen gas that the heat is owing; for the degree of it produced is not proportioned to the degree of condensation; and in many cases, much heat is produced, where the product of the combustion exists even in the aërial form.

Dr Crawford considered this subject under a more just point of view; and it is to his application of a principle laid down by Dr Irvine, that we are indebted for that explanation of the origin of the heat in combustion, which is most conformable to the laws caloric observes.

The law had been established by Dr Black, that different bodies have different capacities for caloric, or, in other words, contain at the same temperature different quantities of that power. It had been shewn by Dr Irvine, that the capacities of bodies are changed by chemical combination, and he had assigned this as the cause of the heat which occurs in some cases of chemical action. The state of chemical knowledge at that period, did not allow him to extend the law to the production of heat in combustion; but from the progress of discovery, as to the nature of the changes which happen in this process, Dr Crawford was enabled to make this application, and, in the course of his researches, to establish it by experiment. It had at that time been established, that a quantity of oxygen gas is consumed by every combustible body in burning; this oxygen, according to the theory then generally maintained, combining with the phlogiston of the combustible matter. Dr Crawford examined by experiment the capacity of oxygen gas for caloric, the capacities of inflammable bodies, and the capacities of the substances formed by their combustion; and the result of these experiments was, that the heat produced in combustion owes its evolution to a change of capacity, and must be derived from the oxygen gas. It was proved that oxygen gas has a large capacity for caloric, or contains a large quantity of it at a given temperature; it was likewise proved, that the capacities of inflammable bodies are comparatively small; from this it followed, that they can furnish little of the caloric disengaged in burning. It was lastly proved, that the capacities of the substances formed by their combustion, are superior to those of the inflammable bodies from which they are formed, but much inferior to the capacity of the oxygen gas, and inferior also to the mean of the capacities of this gas, and of the inflammable matter.—From these facts, it followed, whatever the agency of the oxygen in combustion might be, whether it enters into immediate combination with the combustible body, or with any principle of that body, that an elevation of temperature must attend combustion, and that this must be owing to the diminution of capacity in the substances concerned.

This theory was delivered by the author in the Medical Society of Edinburgh in 1777, a period at least as early as that at which any explanation was given of this phenomenon by Lavoisier; and was published in 1779. In the first experiments which Dr Crawford made to confirm it, he had fallen into considerable errors in the estimation of the capacities. These he rectified, and in 1788 published an enlarged edition of his work,—a work which has been justly characterised, as containing more of the philosophy of heat than any other. The principle of the theory remains the same, and the facts on which it rests are experimentally established. When a change of capacity happens, there must be an alteration of temperature: if the capacity is diminished, the temperature must be elevated, for the bodies suffering that diminution are incapable of containing the whole of the caloric which they before contained. In combustion, it is proved that such a diminution happens, or the substance formed has a capacity inferior to the mean of the capacities of the oxygen gas and the combustible body; and as the capacity of the latter is inconsiderable, compared with that of the former, it is principally the caloric contained in the oxygen gas that must be evolved.

An example from Dr Crawford's table of capacities will place this in a clear point of view. The capacity of oxygen gas is stated at 4.749; the capacity of charcoal at 263, or the oxygen contains a quantity of caloric expressed by the former number, proportioned to what is contained by the charcoal expressed by the latter number, at the same temperature, and in an equal weight. The capacity of carbonic acid,—the product of the combustion of charcoal, is 1.045,—inferior obviously to the mean of that of the oxygen gas and charcoal, but superior to that of the charcoal itself. The quantity of caloric, therefore, contained in the charcoal, is insufficient to supply the caloric which the carbonic acid produced from its burning will contain, and hence what is rendered sensible must be derived from the oxygen gas. This conclusion will become stronger, if we take into account the proportions in which these substances combine together, about 2½ of oxygen being combined with 1 of charcoal, during its combustion. With this entering into the calculation, it can be shewn, as Dr Crawford has stated it, that from the diminution of capacity which attends the burning of charcoal, as much caloric must be rendered sensible as if not dissipated, but applied to the carbonic acid, the product of the combustion, would raise its temperature more than four times the excess of the heat of red-hot iron above the common temperature of the atmosphere *.

Similar examples might be taken from other inflammables; and in all the general principles already stated, will be found to hold just. The only exception is hydrogen gas; its capacity is even superior to that of oxygen, and therefore it must afford much of the caloric evolved in its burning.

Lavoisier considered this subject under a different point of view. In 1777, he had said, that the air contains a quantity of the matter of fire chemically combined with it; that in combustion the gravitating matter of the air combines with the combustible body, and parts with its fire, which appears as heat and light. This explana-

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* Crawford on Heat, p. 402.

tion he retained. He assumes the distinction of free and combined caloric, the former being that portion which produces temperature, the latter that "which is united to a body in such a manner that it cannot be abstracted but by a chemical decomposition; the matter of heat in this state is deprived of its elasticity; it exists in the body, not merely in a state of aggregation, but as a constituent part of it, and is not capable of producing heat*." It is this portion of combined heat, contained in oxygen gas, which is disengaged in combustion; and, as Lavoisier expresses it, its disengagement is owing to the combustible body exerting a stronger attraction than the caloric does to the concrete oxygen; in consequence of this superior affinity they combine together, and the caloric formerly combined in the gas resumes its properties. "A combustible body," says Lavoisier, "is one which has the property of decomposing vital air,—one to which the oxygen has a stronger affinity than to the matter of heat; so that combustion is nothing more than the separation of oxygen from this matter of heat to enter into a new combination†."

The difference between these two explanations is sufficiently evident; in the one the extrication of caloric in combustion is ascribed to a diminution of capacity, while in the other the caloric is supposed to have previously existed in a state of chemical union in oxygen gas, and to be disengaged by the superior affinity of the inflammable body to oxygen. It is thus distinctly stated by La Place.

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* Mémoires de l'Acad. des Sciences, 1783, p. 526.

† Ibid. p. 535.

"M. Lavoisier supposed that the heat disengaged is combined in the pure air, and that that fluid owes to the expansive force of the heat thus contained in it, its aëriform state; while, according to Dr Crawford, the matter of heat is uncombined in the pure air, and is disengaged only because the pure air in combining loses a great part of its specific heat*."

Referring to the observations which have been already made on the hypothesis of combined caloric, (Note B.), it is not difficult to determine which of these modes of explanation is to be preferred. The doctrine of caloric being an element, existing in gases in a state of chemical combination, and producing by such a combination the aëriform state, is an hypothesis unsupported, and probably false. The principle, that different bodies have different capacities for caloric, or contain in equal weights and at equal temperatures different quantities of this power, is demonstrated; it is not even called in question, and is indeed a simple expression of a fact. It is also proved by Dr Crawford, that in combustion the capacities of the bodies concerned are changed, and that the capacity of the product is inferior to the mean of the capacities of the oxygen gas and combustible body. Unless the experiments of Crawford, by which these conclusions are established, are invalidated; or unless it is shewn that the difference in the quantities of caloric contained in different bodies, which is expressed by saying that they have different capacities, is owing to that part of the caloric contained in each above that contained in the others being chemically combined with it, it must be evident, that the language which supposes such a combination involves unnecessarily an hypothesis, and is consequently unphilosophical, while the other is strictly inferred from the phenomena.

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* Mémoires de l'Acad. des Sciences, 1780.

The manner in which Lavoisier expressed his theory on this subject was indeed always loose and incorrect. While he maintained the doctrine of combined caloric, he admits also that of capacity, and defines with Crawford, as he says, "specific heat to be that portion of free caloric necessary to elevate the temperature of a body a certain number of degrees *." Now, this is not Crawford's definition, nor is it conformable to the system he maintains, which does not admit of such a distinction as that of free caloric, the whole caloric in a body existing in that state; and the specific heat being merely the quantity of caloric necessary to raise its temperature a given number of degrees. That different quantities are required for this purpose in different bodies, is a fact which cannot be questioned; that the property by which this law in the distribution of caloric among bodies is observed, is changed by chemical combination, is equally undoubted; that in combustion the change is such that less caloric is necessary to produce a given temperature in the quantity of the substance formed by the combustion, than was necessary to produce the same temperature in the quantities of the oxygen, and the combustible matter which have combined, is likewise proved by Crawford's experiments; it necessarily follows, therefore, that the temperature must be elevated, or a portion of caloric evolved. Now, why should this not

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* Mémoires de l'Acad. des Sciences, 1783, p. 527.

be admitted to be the origin of the heat in combustion, and why should a principle purely hypothetical be advanced to account for it,—that a quantity of caloric exists in bodies in a combined state, and is extricated by a superior affinity? Lavoisier ought either to have denied the doctrine of specific heat, or shewn its deficiency in its application to the explanation of these phenomena. He does neither: he merely neglects it, or rather he mingles in a confused statement * the different causes which might be imagined for the production of heat in combustion; the condensation of the oxygen gas; the change of specific heat; and the disengagement of combined caloric by the exertion of a superior affinity, so as to leave reason to doubt either that he had not formed a distinct idea of the subject, or that he was unwilling to adopt the correct and perspicuous views of Crawford, but wished to preserve to his system at least the appearance of originality.

The system of this latter philosopher has one other recommendation. He justly observes, that it is independent of any hypothesis as to the nature of caloric, or its mode of existence. Whether we consider the temperature of bodies as depending on a peculiar fluid, or whether we consider it as an effect produced by a force inherent in bodies, it must be admitted, that the quantity of this fluid or force may be augmented or diminished in them; that this augmentation or diminution may be rendered greater or less by a communication with surrounding bodies which have a different temperature; that to produce a given temperature in equal quantities of different bodies,

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* Mémoires de l'Acad. des Sciences, 1780, p. 530.

different quantities of this force or fluid are requisite; and that, by chemical combination, a variation in the quantity of caloric necessary to produce a given temperature is required. It is upon these general propositions, which are fully proved, and which are altogether unconnected with any speculations respecting the nature of this power, or the cause of the difference of capacity in bodies, that the evolution of caloric in combustion ought to be explained.

It may therefore, in general, be affirmed, that the extrication of caloric during combustion is owing to a change of capacity in the bodies which combine, the capacity of the compound produced being inferior to the mean of the capacities of the two bodies that have combined; and as the capacity of oxygen gas is greater than that of the inflammable body, we may also affirm, that it is from the former that the caloric is derived. The quantity extricated will be proportioned, other circumstances being equal, to the difference between the capacity of the substance which results from the combustion, and the mean of the capacities of the oxygen gas and the combustible body; the greater that difference is, the greater will be the quantity of caloric rendered sensible. The heat produced by the combustion of different bodies is, however, varied by the quantity of oxygen which combines with them, and the intensity at least of that heat, by the rapidity with which the combination takes place.

Another phenomenon to be explained in the process of combustion, is the extrication of light. While it was believed that light and caloric are essentially the same, or at least modifications of the same substance, the same origin was necessarily assigned to both. According to Stahl, both were extricated from the inflammable body; in the more modern theories of combustion, both have been derived from the oxygen gas. But when this opinion of the identity of light and caloric is not admitted, it becomes necessary to inquire, whence the light evolved during combustion is derived? for it is obvious, that, from the fact of the caloric being disengaged from the oxygen gas, we cannot infer that the light has the same origin, supposing these two principles to be different.

In the system of Lavoisier it seems to be supposed, that the light is a component part of oxygen gas, and that it is from the decomposition of this gas that it appears during combustion.

He always, however, spoke on this subject with reserve. Others of the French Chemists have expressed themselves with less hesitation. Fourcroy, in his Philosophy of Chemistry, gave the following reasons, some of which have frequently been adduced, for believing that the light evolved in combustion proceeds from the oxygen gas. 1st, Combustible bodies afford much more flame when they burn in vital air alone than in atmospheric air. 2d, There are combustible bodies which do not burn with flame, except in vital air. 3d, To disengage the oxygen from bodies which contain it, and convert it into vital air, it is not sufficient to dissolve it in a greater or less quantity of caloric, but it is necessary at the same time to add light. 4th, There are burnt bodies which lose their oxygen on the contact of light alone.

These facts are inconclusive, and it is singular, that they should have been thought of any weight. The first, That combustible bodies afford much more flame when they burn in vital air alone than in atmospheric air, proves nothing. In oxygen gas, combustion is more rapid than in atmospheric air. A greater quantity of the combustible body, as well as of the oxygen, is consumed in a given time; and therefore, whichever of them the light proceeds from, a greater quantity must be extricated. But this affords no presumption whatever, from which of them it is derived. The second fact, That there are combustible bodies which do not burn with flame, except in vital air, is a repetition of the same argument. In atmospheric air, the combustion of many bodies is so slow that the extrication of the light, and even of the caloric, is not perceptible; but in oxygen gas, the combustion being more rapid, the light, whether it proceed from the oxygen or from the inflammable body, is disengaged more suddenly, and must therefore be more perceptible. With regard to the third, it remains to be proved, whether the light added combines with the oxygen or the inflammable body. It may as justly be supposed, *à priori*, in equal conformity to the phenomena, that the light exerts an attraction to the body with which the oxygen was combined, and that in consequence that principle is separated, as that it combines with the oxygen itself. As to the fourth, That there are burnt bodies which lose their oxygen on the contact of light alone, the same observation is applicable: we have no proof given whether the effect is produced by the light exerting an attraction to the inflammable body and combining with it, or by attracting the oxygen, and along with caloric forming oxygen gas.

These facts, then, are equally explained on either supposition, and afford no presumption in favour of the one over the other; neither is there any fact conclusive in support of the opinion, that the light in combustion is derived from the oxygen gas.

It must also be admitted, perhaps, that there is no decisive proof that it is disengaged from the inflammable body: still there are considerations which render it probable that it is a principle of combustibles, and that from them it derives its origin.

Thus, when the compound of oxygen with another body is heated with an inflammable substance, it frequently happens that the oxygen is transferred from the former to the latter, and there is a production of light. But it appears evident that this light could not be derived from the oxygen; for supposing it to be a component part of oxygen gas, it must have been disengaged during the first combination. An example will render this evident. Iron, zinc, antimony, or arsenic, according to Fourcroy, burn with the emission of light when heated in contact with oxide of mercury. Now, when the oxygen first combined with the mercury, its light would be disengaged in the same manner as in other combinations of this kind; there is no reason to presume, therefore, that light exists in oxide of mercury, and the light apparent in these cases must be derived from the metal with which the oxide is heated.

There are many cases of a similar kind. When sulphur is burnt with oxygen, a great quantity of light is disengaged, and a peculiar acid, named the sulphuric, is formed. We have no reason to believe that this acid contains any light. But when it is poured on certain inflammable bodies, such as the essential oils, these are oxidated by attracting its oxygen, and a vivid flame is sometimes suddenly produced. This light must of course have pre-existed in these oils.

A number of deflagrations, in which oxygen is tranferred from a body with which it is combined, to another inflammable substance, and in which there is a production of light, afford a proof of a similar kind.

But the least equivocal proof of the existence of light in combustible bodies, is derived from a fact observed by Scheele, and afterwards made the subject of experiment by the associated Dutch Chemists,—that when mixtures of sulphur with iron, zinc, or other metals, are exposed to a high temperature, the sulphur and the metal combine, and at the moment of their combination, an emission of light, in some of them vivid, and continuing a considerable time, takes place. In this case there is no oxygenation, as is proved by the resulting substance, being a compound of sulphur, with the metal employed: the experiment succeeds also, as the Dutch Chemists found, when the mixture is heated *in vacuo*, or in a tube containing nitrogen or hydrogen gas: The light, therefore, must be derived from one or both of these inflammables; it must be considered as a constituent principle of them, and if light is rendered sensible during their combination with oxygen, it is from this source that it must be derived.

Since there are thus proofs that light is a constituent principle of inflammable bodies, and no proof equally conclusive that it is contained in oxygen gas, the just inference is, that the light disengaged during combustion is derived from the combustible matter. At the same time the relations of light to other bodies are so far peculiar, that nothing more than a probable conclusion can be drawn. It is possible, that it may also proceed from the oxygen gas, though, as this is not proved, it is unnecessary to make the assumption, since a different origin of it, supported by proof, can be assigned.

This opinion with respect to the origin of light in combustion was first maintained by Macquer, though not by any conclusive arguments; it was afterwards adopted by Gren, and indeed is an opinion which must, at the first view of the phenomena, occur as sufficiently probable. Some have affected to consider it as a modification of the doctrine of Stahl,—light being substituted for phlogiston. This, however, is merely a verbal alteration. Lavoisier himself admitted that it was uncertain whence the light in combustion proceeded, and that it was possible it might come from the inflammable body: and the admission that it does so, does not alter one principle of the general theory, nor has it any claim to be regarded even as a modification of it.

A phenomenon somewhat interesting with regard to the emission of light in combustion, is the order in which the different prismatic rays are extricated. This appears to be considerably influenced by the temperature. Those bodies which burn at a low temperature, and do not raise their temperature high by their combustion, as ardent spirit or sulphur, emit the indigo and blue rays most copiously; charcoal, which requires a higher temperature, gives the red rays in greatest abundance; and in all cases where the combustion is rapid, and the heat intense, the rays are expelled in the due proportion which constitutes white light. Mr Morgan supposes [*], and the supposition is sufficiently probable, that this is owing to the different forces of attraction by which the different rays are retained by the inflammable body,—those which are retained by the weakest force, which, if this hypothesis be just, must be the indigo, will be expelled at the lowest temperature; in proportion as the repulsive agency is augmented by the rise of temperature, the other rays will be thrown off, until the temperature is raised so high that the attraction of all the rays is much weakened, when the white light will appear. On this principle may perhaps be also explained the different coloured lights with which the same combustible may be made to burn when different bodies are combined with it, as in the example of alkohol holding different salts in solution. At the same time there is an objection, as Dr Price remarked, to Morgan's hypothesis, that the least refrangible rays are those supposed to be retained by the strongest attraction, while the very property of inferior refrangibility seems to imply a less force of attraction between these rays and the bodies by which they are attracted. The kinds of attraction in these cases might be supposed to be different, though not perhaps with much probability.

Very different quantities of light are emitted by different combustibles. In general it is greatest from those which are volatile, or which, while burning, are in the state of vapour, as is exemplified in oil or wax compared with charcoal, or in zinc among the metals: this circumstance, however, is not essential, as is evident from the bright light given by the combustion of phosphorus, or by iron when burnt in oxygen gas.* It will probably be in a great measure dependent on the relative proportions of light in different combustibles, and the force of attraction with which they may retain it; and is no doubt influenced by the rapidity of the combustion, or the quantity of combustible matter burned in a given time.

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[*] Philosophical Transactions, vol. lxxv. p. 190.

I may add with regard to the theory of the production both of heat and light in combustion, that some doubt must be attached to it, as we know not precisely the relation of these powers to the galvanic principle, nor how far the operation of this is concerned in the process. This is a subject on which at present no speculation that is satisfactory can be advanced, and which must be elucidated by farther discovery.

We have hitherto considered the simplest case of the combination of oxygen with other bodies. There are others more complicated; those in which the oxygen is transferred from one body to another.

Deflagration is one of the most striking examples of this kind. When a quantity of nitre, (nitrate of potassa), is mixed with an equal weight of sulphur, charcoal, or almost any other inflammable body, if the mixture is thrown into a crucible heated to redness, a vivid combustion is instantly excited.

The general explanation of this operation, named by the chemists Deflagration, is sufficiently evident. Nitre is a salt formed by the union of nitric acid and potassa; nitric acid consists of oxygen and nitrogen;—the solid salt, therefore, the nitre, contains a large portion of oxygen, and this oxygen is in such a weak state of combination that it is separated by exposure to a red heat. When, therefore, the mixture of the nitre and of the inflammable body is thrown into the heated crucible, the oxygen of the former is disengaged; it is suddenly presented to the inflammable body, and hence the vivid combustion that is excited; and for the production of this, it is not even requisite to raise the temperature so high as that which would be necessary, if applied alone, to decompose the nitre, the affinity of the inflammable body to the oxygen of the nitre causing it to take place at a temperature somewhat lower. The nitrogen, the other constituent principle of the nitric acid, passes off in the state of gas; and the potassa with which the acid was united, remains mixed, or united with the body formed by the combination of the oxygen and the inflammable substance.

Any other salt containing the nitric acid has the same effect, as well as those which contain another acid, the oxymuriatic acid, all these salts yielding a large quantity of oxygen by the application of heat.

But though the general theory of this operation is thus sufficiently evident, it has been supposed that the more minute explanation of its phenomena, particularly of the extrication both of light and caloric which accompany it, is attended with considerable difficulty.

It has been observed, that during combustion, the caloric which is evolved is reasonably supposed to be derived from the oxygen gas, since the general truth is sufficiently established, that bodies in the gaseous form contain much more caloric than those that are fluid or solid, and consequently it may be concluded, that when oxygen gas by combining with another body passes to the solid state, a large quantity of caloric must be rendered sensible. But in deflagration, the oxygen which combines with the inflammable body is already in a solid state;—it is not combined with caloric in the form of gas, but is merely transferred from one solid base to another, and frequently even thus passes into an aëriform product. Whence then does the caloric proceed, which is extricated during this process?

To lessen this difficulty, it must be observed in the first place, that in the consumption of a given quantity of oxygen by deflagration, less caloric is evolved than in the consumption of the same quantity by combustion. This may be calculated from the experiments of Lavoisier and La Place *. Sixteen ounces of nitre contain about 6½ ounces of solid oxygen. This quantity of nitre, deflagrated with charcoal melted in the calorimeter 12 lbs. of ice, which is in the proportion of 29½ lbs. of ice melted by the consumption, by deflagration, of each pound of oxygen contained in nitre. But each pound of oxygen in the gaseous form, when burnt with charcoal, melts 37½ lbs. of ice, and consequently the quantity of caloric disengaged during the consumption of a given quantity of oxygen by deflagration, is considerably less than that disengaged by the consumption of the same quantity by combustion.

Still from these experiments it appears that the quantity of caloric evolved is considerable. It has been ascertained, however, that when oxygen is combined with nitrogen, to form nitric acid, a smaller quantity of caloric

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* Mémoires de l'Acad. des Sciences, 1780, p. 378—400.

is disengaged than in other combinations of oxygen. And again, when nitric acid is combined with potassa, to form nitre, a very inconsiderable quantity of caloric is disengaged. It is certain, therefore, however it may be explained, that a large quantity of the caloric contained in oxygen gas remains in the nitre, and it is this caloric that is extricated during deflagration. Of those other salts which contain oxygen in large quantity, and combined in them by a weak attraction, such as the oxymuriate of potassa, and which have a similar power of deflagrating with inflammable bodies, the theory of their operation is the same. These salts readily part with their oxygen to the inflammable matter; and this oxygen, as it exists in them, retains a large quantity of caloric, which is set free during the deflagration. Lavoisier remarks, with respect to all these salts, that it is owing to the presence of this large quantity of caloric that they are so easily decomposed by heat, and part with their oxygen so readily.

It is difficult to determine whether this large quantity of caloric, which there can be no doubt is retained by oxygen in passing into these combinations, is retained in them by chemical combination, or merely by their capacity being unusually large, as there is much difficulty in ascertaining the capacities of these bodies with accuracy. Were it proved, as has been alleged, that the capacity of nitrate of potassa is not great, and that the united capacities of that salt and charcoal are inferior to the united capacities of the products of the deflagration of these substances, though it would not invalidate the above facts, it would furnish the strongest argument against the opinion that caloric exists in bodies in proportion solely to their capacities. But the difficulty of the experiments must render the conclusions uncertain; at least this applies to any which have hitherto been made; and, in drawing such conclusions, it would also be not less requisite to attend to the proportions of the substances concerned in the deflagration, which has not been done.

The origin of the light disengaged in deflagration, must be explained in the same manner as in other cases of combustion. If the opinion be maintained, that it is a component principle of combustible bodies, it will be extricated in deflagration from the inflammable body; while, if it be a constituent principle of oxygen gas, it may still be derived from this source; for when oxygen unites with nitrogen, no light is extricated, and therefore if oxygen gas do contain light, this light must remain combined with it, as it exists in the nitrate of potassa.

A peculiar phenomenon attends deflagration arising from the nitrogen gas, which is expelled from the decomposition of the nitre. If the mixture of the nitre and of the inflammable body be compressed in a metallic tube, and kindled by a spark, the nitrogen gas being instantly disengaged by the deflagration, and its elasticity being increased by the caloric, a violent explosion takes place. When the inflammable substance is one which, with oxygen, forms a compound that assumes the gaseous form, charcoal for instance which forms carbonic acid gas, another powerful explosive agent, is introduced, and the force both of this and of the nitrogen gas is greatly augmented by the caloric set free at the same time. It is on these circumstances conjoined that the great explosive force of gunpowder depends.

This constitutes what in chemical language is termed Detonation. Deflagration is the rapid combination of concrete oxygen with an inflammable body, accompanied with the emission of light and caloric. Detonation is the same combination effected still more suddenly, and with an explosion of more or less force.

When the inflammable substance, and the salt containing the oxygen, are inclosed in a tube, and pressed down, it is not difficult to perceive that when they are ignited, an explosion must take place from the sudden extrication of the gaseous products, and the resistance by the tube. But there are many instances of detonation, in which there is no resistance of this kind, in which the detonating substances are merely rubbed together, or struck by a hammer. In such cases, the detonation is to be ascribed to the friction or percussion approximating the particles of the inflammable body and the oxygen, whence their instantaneous combination, and the formation of an aëriform product, the elasticity of which is much augmented by the extrication of caloric from the combination, and which, striking against the surrounding atmosphere, causes the report. The mixtures most favourable for such detonations are those of salts in which oxygen is present, retained by a weak affinity, and retaining much of its caloric, and of an inflammable substance having a strong attraction to that oxygen, and disposed to volatility, or to form with oxygen an aërial product.

The last case of the general agency of oxygen to be explained is, that where it is transferred from one body to another, without being accompanied by the phenomena of combustion. Thus oxygen is contained in all acids. When an acid is poured on an inflammable body, it often happens that the latter is able to decompose the acid, by attracting its oxygen, when of course the substance thus deprived of oxygen is disengaged. In this case, the extrication of caloric which takes place is not considerable. This is owing partly to the oxygen, as it exists in the acid, having been deprived of part of its caloric, and partly to the product of the decomposition absorbing another portion of caloric. The process goes on, too, comparatively slowly, and therefore the caloric disengaged is less perceptible than if it were extricated in a shorter time. Neither does any disengagement of light attend this process, because it enters into a state of new combination; if it leave the inflammable body, it will combine with the base of the acid, which returns to its original state. In some cases, however, part of the light is rendered sensible.

Water likewise affords the oxygen it contains to some inflammable bodies, especially to some of the metals, and the phenomena are similar to those produced by the action of the acids, the hydrogen, the other constituent principle of the water, being separated, and no light and little caloric being extricated. The process goes on very slowly at a natural temperature, but is more rapid at a red heat, or at a low temperature when it is aided by the affinity of an acid.

The combination of oxygen with a body, whatever may be the phenomena attending it, is termed in general its Oxidation or Oxygenation. These terms have been objected to by Mr Chenevix, as the syllable *ate* is appropriated in the new nomenclature to denote acids or compounds in which acids exist. Hence he proposed Oxidizement and Oxygenizement; a change which has been adopted. The two terms, according to either nomenclature, are not quite synonymous, as I shall immediately have to point out.

The compounds of oxygen possess some common properties, and agree to a certain extent in the chemical agencies they exert. Hence they admit of some general observations.

When the compound which results from the union of oxygen with a body, has a sour taste, is capable of reddening the vegetable colours, and of combining with the alkalis, so as to neutralize the alkaline properties, it is named in chemical language an Acid. There are a number of Acids, or of substances possessing these properties, and these, so far as they have been analyzed, contain oxygen. Hence this element is considered as the principle of acidity, and from this indeed the name Oxygen has been derived.

Acidity, however, is not the invariable result of the combination of oxygen. On the contrary, the products of these combinations are often destitute of any acid property. It is convenient to have a term to denote this class of compounds, and accordingly in the modern nomenclature they are denominated Oxyds, or, as the name should be written, Oxides.

Oxides and Acids, then, are two orders of compounds, under which are arranged all those substances that result from the combination of oxygen with other bodies. Acids are distinguished by the possession of certain common properties just now enumerated. Oxides have scarcely any common qualities by which they are distinguished; the distinction being rather negative, or denoting that the compound has no acid power. The alkalis and earths are now to be regarded as oxides, and the most distinguishing property common to them, and likewise to all the metallic oxides, is that of neutralizing the properties of acids. But there are likewise oxides to which this property does not belong. The word oxidation or oxidizement is used, in strict propriety, to denote that combination of oxygen where the resulting compound is not an acid, but an oxide. Oxygenation or oxygenizement is a more general term, expressing every combination of oxygen.

Many substances are capable only of oxidizement. Thus the greater number of the metals are capable of combining with oxygen. These compounds are generally oxides; nor, with the exception of two or three metals, by any addition of oxygen, can they be made to acquire any acid property. Hydrogen unites with oxygen only in one proportion, and forms water, which is not acid.

There are other inflammable substances, again, which are capable of combining with oxygen, forming in one proportion an oxide, and in another an acid. In general, the first degree of oxygenizement forms an oxide, and this by combining with a larger proportion of oxygen forms an acid. Thus nitrogen united with nearly two parts of oxygen, forms a substance, which having no acid property, is an oxide of nitrogen, while, united with four parts of oxygen, it forms an acid compound. The case is the same with a number of other bodies; there are one or two, however, where, after an acid has been produced, the addition of more oxygen diminishes or destroys the acid properties; and there are some perhaps which form acids even in the first stage of oxygenizement; at least their existence in the state of oxide is doubtful. But, in all those substances, which, by combining with oxygen in different proportions, produce both oxides and acids, the oxide is invariably the product of the first stage of oxygenizement, and the acid results from the addition of a larger proportion of oxygen. In some cases, the same substance too is susceptible of different degrees of oxygenizement, so as to form two acids different in their properties from each other; the one, from the larger proportion of oxygen, being usually the most energetic in its action.

The general properties of those compounds of oxygen which can be formed into orders,—the acids, alkalis and earths, will be considered under the chemical history of these substances.

BOOK II.

OF WATER AND ITS BASE.

WATER was long regarded as a simple substance, and in the system of ancient philosophy was considered as one of the elements from the union of which all bodies were supposed to be formed. The discovery of its production by the union of two aëriform fluids, one of the most splendid and important of modern chemistry, was reluctantly admitted, and not until it appeared to have been established by the most decisive evidence.

The composition of water was inferred, not from its analysis, but from synthetic experiments, in which it appeared to be formed by the union of its constituent parts. It had been long known to the chemists, that an air or vapour is disengaged in certain processes, particularly in the solution of some metals in dilute sulphuric or muriatic acid highly inflammable, which burned, when kindled at the orifice of the phial from which it was disengaged, and which exploded with violence when previously mixed with atmospheric air. Mr Cavendish first fully examined its properties, and proved it to be a distinct substance; he gave it the name of Inflammable Air.

This air had been fired by Macquer in a glass vessel in 1776, and he observed that some drops of a clear fluid were condensed, which appeared to him to be nothing but pure water. Lavoisier, the succeeding year, made a similar experiment, and by introducing lime-water into the vessel, immediately after the combustion had ceased, he ascertained that no carbonic acid was produced, as some had supposed. He repeated this experiment in 1781, and found that no acid whatever, the production of which his theory had led him to expect, was formed. Priestley too fired mixtures of hydrogen with oxygen, and observed the deposition of water, without discovering its origin.

It was at length concluded, nearly about the same time, by Mr Watt and Mr Cavendish, that water is a compound body, formed from the combination of oxygen and hydrogen ; and this conclusion being apparently established by all the evidence which the science admits, has been received into the modern system of chemistry. The chemical history of one of its elements, oxygen, having been already given, as a principle of atmospheric air, that of its other element or base, hydrogen, only remains to be delivered, prior to the history of water itself.

CHAP. I.

OF HYDROGEN.

THIS substance naturally exists in the aërial form. The chemists, at an early period, it has been observed, were acquainted with its production in some chemical processes, and with its distinguishing property,—its inflammability. Van Helmont from this property had given it the name of Gas Igneum; and it had attracted the attention of Boyle, Mayow and Hales. It is to Mr Cavendish, however, that we are indebted for the first accurate account of its production and properties *. He gave it the name of Inflammable Air. From being considered as the base of water, it received, at the framing of the new nomenclature, the name of Hydrogen.

This gas is always obtained from the decomposition of water, as it cannot, from other substances in which it exists, be easily disengaged in perfect purity. Some substance is made to act on water, which exerts an attraction to the oxygen without combining with the hydrogen, when of course the hydrogen is disengaged, and passes into the elastic form.

At the common temperature of the globe, this decomposition cannot be effected with rapidity by any single affinity. Iron moistened with water decomposes it very slowly, and evolves hydrogen; but at the temperature of ignition the decomposition is more rapid. If a coil of iron-wire or a quantity of iron-filings be put into an iron or coated glass or earthen tube, which is placed across a small furnace, and surrounded with burning fuel so as to be brought to a red heat, on distilling water from a retort connected with it, the vapour in passing over the surface of the ignited iron is decomposed, the iron attracts its oxygen, and hydrogen gas issues from the extremity of the tube.

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* Philosophical Transactions, vol. lvi. p. 141.

This process is a troublesome one, and by the agency of an acid, water is decomposed as rapidly by iron or zinc at a natural temperature. Zinc affords the hydrogen in greatest purity. One part of it in small pieces is put into a retort, or a bottle with a bent tube adapted to it; two parts of sulphuric acid previously diluted with five times its weight of water are poured upon it; an effervescence is immediately excited, hydrogen gas escapes, and is to be collected in jars filled with water, and placed on the shelf of the pneumatic trough. Its disengagement continues until the zinc is dissolved. Iron may be employed in place of zinc, but containing generally a little carbon, which is dissolved by the hydrogen, it affords a gas less pure. Muriatic acid serves the same purpose as sulphuric acid, but must be diluted with only two or three times its weight of water.

In this experiment the hydrogen gas is derived entirely from the decomposition of the water, the oxygen of which is attracted by the metal. That the acid suffers no decomposition, is proved by the liquor at the end of the experiment being capable of saturating as much of an alkali as the quantity of acid employed would have done in a pure state. The agency of the acid was formerly explained on the absurd doctrine of disposing affinity,—that it had no attraction to the pure metal, but to the oxide of the metal; that to satisfy this affinity it caused the oxidation of the metal at the expence of the water, and then combined with the oxide thus formed. In conformity to Berthollet's speculations, it may be referred to the affinities of the acid to iron, and to oxygen, conspiring with the affinity of iron to oxygen. These co-operating produce a ternary combination while the hydrogen gas is disengaged. It may, perhaps, be considered as an objection to this explanation, that there is no proof that sulphuric acid exerts such affinities. In the chapter on Affinity, I have endeavoured to shew the probability of the inference, That all bodies have mutual attractions, which in particular cases are not apparent, from their being counteracted by cohesion, elasticity, or other circumstances; but which always are to be regarded as forces which in some degree do act, and the effect of which, when two or more such affinities co-operate, as they may be supposed to do in the present case, may become apparent.

Hydrogen gas is permanently elastic. When collected over water, it is observed to have a peculiar smell, slightly fœtid, which is not so perceptible when it is collected over quicksilver, and which is lost when the gas is exposed to substances which powerfully attract humidity. It is not the only substance in which water appears requisite to develope odour.

This is the lightest of the gases, and indeed the lightest substance whose gravity can be ascertained by weighing. Its specific gravity varies considerably, according to its state with regard to humidity. When it has been transmitted through water, or has remained for some time exposed to it, it is about 10 times lighter than atmospheric air; when it has been received over quicksilver, and exposed to any substance which attracts water strongly, as quicklime, it is nearly 13 times lighter, or atmospheric air being 1000, is 84. Its specific gravity in this state, water being 1.0000, is stated by Lavoisier at .0000946. 100 cubic inches weigh 2.613 grains. It is from this levity that it has been applied to the construction of balloons, a varnished silk or linen bag filled with it having a specific gravity so much less than atmospheric air, as not only to rise in the atmosphere, but also to elevate an additional weight.

The chemical property by which hydrogen gas is most eminently distinguished, is its great inflammability. When an ignited body is approached to it in contact with the atmosphere, it is immediately kindled, and continues to burn while the air is admitted ; if previously mixed with atmospheric air, and a burning body approached to the mixture, or an electric spark sent through it, it instantly inflames with detonation ; and when it has been mixed with oxygen gas, the detonation is more violent. When burning at the extremity of a capillary tube, on bringing a wide tube over the flame, a singular phenomenon, accidentally observed by Dr Higgins, is produced, that of sounds of various tones, which vary in acuteness and strength, according to the width, the length of the tube, and the kind of substance of which it is formed,—owing apparently, as Pictet and De la Rive have explained it, to the vibrations excited in the matter of the tube by the rapid expansion and condensation of the watery vapour near and around the flame, and which, regulated and equalized by regular reflections from the sides of the tube, constitute a musical sound *.

From its inflammability hydrogen gas has been applied to the purpose of eudiometry. A given measure of it is put into the tube, Fig. 58. with a quantity of the air de-

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* Nicholson's Journal, 8vo. vol. i. p. 129. ; Ibid. vol. iv. p. 23.

signed to be submitted to trial, and is inflamed by the electric spark, the diminution of volume indicating the quantity of oxygen. This is the method of Volta: 100 measures of oxygen require rather less than 200 measures of hydrogen for saturation; about 40 measures of hydrogen are, therefore, sufficient to saturate the oxygen contained in 100 measures of atmospheric air, but it is proper to use an excess of hydrogen, as otherwise part of the oxygen is liable to escape combination. From 60 of hydrogen with 100 of atmospheric air, Mr Dalton states, that the residuum after explosion is 100, 21 of oxygen combining with 39 of hydrogen. The method is simple and expeditious, and as Humboldt and Gay Lussac have remarked, has the advantage, from the bulk of the mixture and the great diminution of volume from the consumption of a given quantity of oxygen, of being more delicate than any other. It also requires no corrections for variations of temperature or atmospheric pressure; and any impurity in the hydrogen gas, which it has been supposed might be a source of error, may be avoided by care. It is not, however, without its disadvantages. It is more troublesome than some other eudiometrical methods; and there is a source of error noticed by Biot, that the pressure from the detonation forces out some bubbles of air from the water over which the experiment was made, and adds to the volume of the residual air *. It affords, however, the best method of determining the purity of oxygen gas, or the proportion of oxygen in any mixed gas containing it in considerable quantity. Humboldt and Gay Lussac, in an elaborate

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† Nicholson's Journal, 8vo, vol. xviii. p. 128.

memoir, have pointed out all the circumstances to be attended to in employing it as an eudiometer *.

Though hydrogen gas be inflammable, it is incapable of supporting the combustion of other inflammables. If a burning body be quickly immersed in it, it is immediately extinguished.

This gas is incapable of supporting animal life by respiration; an animal immersed in it is soon killed. It does not, however, appear to be so positively deleterious as the other noxious gases. Scheele long ago observed that he was able to breathe it for 20 inspirations †. Fontana shewed, what Scheele indeed had observed, that if the lungs were previously emptied as much as possible of atmospheric air, by a forcible expiration, it cannot be breathed so long, though still it did not appear to him to be positively deleterious, like some of the unrespirable gases ‡. Rosier, even after expelling the air from the lungs, breathed hydrogen gas for several respirations; and Mr Davy, in his experiments on the respiration of the gases, remarked that in one experiment, after a complete exhaustion of the lungs, he found great difficulty in breathing hydrogen for half a minute, though in a subsequent experiment, with the same preparation, he breathed it for near a minute. The first six or seven inspirations produced no sensations whatever; in half a minute, a sense of oppression was felt at the breast, which increased until the pain of suffocation interrupted the ex-

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* Journal de Physique, t. lx. p. 129.

† Treatise on Air and Fire, p. 160.

‡ Opuscules Physiques, p. 2.

periment *. Hydrogen, therefore, is incapable of supporting life; the respiration of it can be continued only for a short time, and animals confined in it soon die. It appears only to prove fatal, not by a positively noxious quality, but by excluding atmospheric air, the due supply of which by respiration is indispensable to life. Blood exposed to it acquires a deep black colour, and the gas suffers a diminution of volume.

Hydrogen is not, as several of the other gases are, noxious to vegetable life; at the same time it appears to contribute little to the nourishment of plants, Dr Priestley having found that it still continued inflammable after a growing vegetable had been confined in it for several months. It can apparently supply, to a certain extent, the place of light in supporting vegetation. Van Humboldt observed that some cryptogamic plants in mines, and of course secluded from light, were not pale, but of a green colour, such as they would have had from growing under exposure to the light of day; and he concluded with sufficient probability, that the agency of light had in this case been supplied by the hydrogen gas which is evolved in greater or less abundance in such situations.

Hydrogen gas is so sparingly soluble in water, that when agitated with it, it suffers no perceptible diminution of volume. When the water has been previously freed from atmospheric air, Mr Henry found that 100 cubic inches take up 1.5 of the gas under a common atmospheric pressure; under increased pressure, a larger

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* Chemical Researches, p. 400, 466.

quantity, equal to one-third of the volume of the water, is absorbed.

The affinities of hydrogen seem principally exerted towards inflammable bodies. It unites with sulphur, phosphorus and carbon, and forms gaseous compounds; it appears to be capable of dissolving even some of the metals, particularly iron, zinc and arsenic. United with nitrogen, and a portion of oxygen, it forms one of the alkalis, ammonia; with oxygen alone, water. It is also a constituent principle of the greater number of the vegetable and animal products.

Hydrogen gas may be regarded as a product of some natural operations, not indeed perfectly pure, but forming at least the predominating ingredient in certain inflammable gases, generally in combination with carbon. In this state it is sometimes collected in mines, being known to the miners by the name of Fire Damp, and is often the cause of accidents, from exploding on the approach of an ignited body. It is also extricated from stagnant water, and from marshy situations, from the slow decomposition of vegetable and animal substances, holding dissolved not only carbon, but probably other substances, and forming, as has been supposed with some probability, gases which render the air of such places unhealthy. From its levity it has been supposed that the quantity of it produced at the surface of the earth will rise through the atmosphere and occupy the higher regions, and on its presence some of the phenomena of meteorology, particularly the sudden appearance of some fiery meteors, have been imagined to depend.

The present discoveries in chemistry promise to throw some light on the nature of hydrogen. A very singular fact has been established, which suggests the conclusion, that its base or gravitating matter is of a metallic nature; in other words, that hydrogen gas is a metal in the aërial form. Ammonia, one of the alkalis, is a compound of hydrogen and nitrogen, with a portion of oxygen. The Swedish Chemists, Berzelius and Pontin, operating on this substance, discovered that when quicksilver, negatively electrified in the galvanic circuit, is in contact with a solution of ammonia, it increases rapidly in volume, acquires consistence, and, when it has increased to four or five times its original dimensions, becomes a soft solid. As these changes can scarcely be supposed to be produced in the quicksilver, but by its having combined with a quantity of metallic matter, this interesting experiment appears to establish the conclusion, that the base of ammonia, which, according to the view above stated, is a compound one, consisting of hydrogen and nitrogen, is of a metallic nature, and that by the operation of galvanism, and the affinity of the quicksilver, the oxygen combined with this base had been abstracted, and the quicksilver and base had combined. Accordingly, what confirms this conclusion, these chemists found, that when this new substance is exposed to the air, oxygen is absorbed, ammonia is formed, and the quicksilver reproduced. Or, if dropt into water, ammonia is also formed; the quicksilver resumes its former state, and, from the decomposition of part of the water, to afford oxygen to the metallic matter of the ammonia, a portion of hydrogen is evolved.

Mr Davy repeated the experiment, and obtained the same results, as he did also by diversifying the operation in various ways. He farther de-oxidized ammonia by the action of the base of potassa, or of soda, and obtained the metallic matter in combination with quicksilver. He did not succeed, however, in any of the methods to which he had recourse in decomposing this compound, so as to obtain alone the substance derived from the ammonia, and combined with the mercury. That it is of a metallic nature, however, may be inferred with every probability. The quicksilver was enlarged in volume, thickened, and at length rendered solid, preserving at the same time its metallic lustre and properties. And reasoning from every analogy, no substance but one of a metallic nature could produce such effects.

Is this substance derived from the hydrogen or nitrogen of the ammonia or both, and are these gases, metals in the aërial form? Or are they oxides in this state, and become metals by de-oxidation? The subject must yet remain undetermined; but if the relation between hydrogen and nitrogen, already stated under the history of the latter substance, that it is an oxide of hydrogen, be just, then hydrogen in its aërial form must either be metallic, or at least have a metallic base, and the substance combined with the quicksilver in the above experiments must be this metal.

Mr Davy has even given a view, at present professedly hypothetical, but not without probability, which extends farther the relations of hydrogen. He has supposed, that, instead of being itself metallic, it may form metals; that it may be the common principle of metals and inflammables, being combined in each with certain bases; and under this point of view, it will stand in opposition to oxygen. This receives some support from the apparent relations of those principles to the different electrical states. "Oxygen is the only body," Mr Davy remarks, "which can be supposed to be elementary, attracted by the positive surface in the electrical circuit; and all compound bodies, the nature of which is known, that are attracted by this surface, contain a considerable proportion of oxygen. Hydrogen is the only matter attracted by the negative surface, which can be considered as acting the opposite part to oxygen: may not then the different inflammable bodies, supposed to be simple, contain this as a common element?"

On this subject, other speculations might no doubt be advanced, but, as Mr Davy has justly observed, not much importance can be attached to them. "The age of chemistry is not yet sufficiently mature for such discussions; the more subtile powers of matter are but just beginning to be considered; and all general views concerning them must as yet rest upon feeble and imperfect foundations *."

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* Philosophical Transactions, 1808.

CHAP. II.

OF WATER.

WATER, it has been stated, appears when hydrogen is made to burn; and when oxygen is abstracted from water by substances having a strong affinity to that element, hydrogen is evolved, and assumes the elastic form. The conclusion appears, therefore, necessarily to follow, that water is a compound of these two gases.

This conclusion with regard to the composition of water, I have observed, was drawn nearly at the same time by Watt and by Cavendish; the memoirs of these philosophers on this subject having been published in the same volume (the 74th) of the Philosophical Transactions.

It was suggested to Mr Watt by some experiments of Dr Priestley, in which metallic oxides were reduced to the metallic state, by being heated in hydrogen gas; and others in which, when mixtures of hydrogen and oxygen gases were fired in close vessels, moisture was deposited, without any other sensible product; and this moisture, when wiped off, and absorbed by a sponge, was found equal to the weight of the gases employed. Since water is thus the only sensible product of the combination of the two gases, (besides the heat and light which are disengaged), are we not, says Mr Watt, authorised to conclude that it is a compound resulting from their union, or (conformable to the opinion, then maintained, that hydrogen is phlogiston,)—a compound of phlogiston and oxygen?

The attention of Mr Cavendish was likewise directed to this subject, by Dr Priestley's experiments on the burning of hydrogen ; and in order to discover the product, he burnt large quantities of this gas. In one experiment, 500,000 grain measures of hydrogen gas were burnt slowly, with about 2½ times the quantity of common air, and the current of air made to pass through a cylinder of glass, in order to deposite the dew. Upwards of 135 grains of water were thus condensed in the cylinder, which had no taste nor smell, which left no sensible sediment, when evaporated to dryness, nor gave any pungent smell during the evaporation ; which, in short, seemed to be pure water. This being the only sensible product of the combination of hydrogen and oxygen, Mr Cavendish considered it as a compound, formed by their union.

The experiment of burning hydrogen gas was made the same year by Lavoisier, who was informed at the same time by Dr Blagden, of the experiment having been made by Mr Cavendish, of the result, and the conclusion drawn from it ; and so far was he from having conceived an idea of this discovery, that, as Mr Cavendish has stated, " until he was prevailed upon to repeat the experiment himself, he found some difficulty in believing, that nearly the whole of the two airs could be converted into water *." He obtained nearly 5 drachms of water perfectly pure †. Monge made a similar experiment, and found that the quantity of water procured is equal to the quantity of the gases which disappear ; and in a subsequent experiment,

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* Philosophical Transactions, vol. lxxiv. p. 134.

† Mémoires de l'Acad. des Sciences, 1781, p. 473.

which Lavoisier made assisted by Meusnier, he inferred that the oxygen and hydrogen combine to form water, in the proportions of 13.1 of the former by weight to 86.8 of the latter. They also established its composition, by decomposing it, by substances which attract its oxygen, and disengage hydrogen gas, as well as by a reference to the experiments of Priestley, in which some of the metallic oxides were reduced by that gas, assisted by heat *.

The discovery of the composition of water, besides its intrinsic importance, derived an adventitious consequence, at the time it was made, from its connection with the explanations of the antiphlogistic doctrine, which were at that time warmly contested. It was known, that during the solution of metals in certain acids hydrogen gas is disengaged ; it had been observed by Dr Priestley, that some of the metals, when exposed to an intense heat, gave out a quantity of hydrogen gas ; and that when several of the metallic oxides were heated with this gas, they were reduced to the pure metallic state, without any oxygen being afforded by this reduction. These facts were inexplicable on the antiphlogistic system ; it could give no account of the origin of the hydrogen in the one case, nor of its disappearance in the other in which the reduction of the metallic oxide was effected. The opponents of this system considered these facts as demonstrating its fallacy, and they concluded, that hydrogen was the phlogistic principle ; that it was a component part of the metals, as well as of other inflammable bodies ; and hence the explanation of its action in these cases, as well as in many

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* Mémoires de l'Acad. des Sciences, 1781, p. 478.

others, in which hydrogen was produced. The discovery of the composition of water at once solved these difficulties, since it explained the origin of the hydrogen in the one case, and the mode in which it operated in the other. The reality of this discovery was hence for a while disputed, and there were certain ambiguous circumstances in the experiments that afforded room for doubt.

The principal circumstance of this kind, was the apparent production of an acid during the combustion of the hydrogen; the water condensed being frequently very sensibly acid, as was observed by Mr Cavendish. It was therefore concluded, that this acid was the real product of the combustion, and that the water collected was the portion that had been held by the gases in solution.

By farther investigation, however, these difficulties were removed; and, indeed, even previous to the objection having been made, the principal circumstances from which the production of acid arises had been pointed out by Mr Cavendish, and their operation explained *.

The acid formed was found to be the nitric. Now, this acid is a compound of oxygen and nitrogen; and as it is difficult to procure oxygen gas free from a small admixture of nitrogen, it was urged that the small quantity of nitric acid occasionally contained in the water, might be derived from the combination of oxygen with a part of the nitrogen present in the gases.

It was accordingly found, that this production of nitric acid might be regulated at pleasure. Nitrogen does not combine with oxygen so readily as hydrogen does; if,

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* Philosophical Transactions, vol. lxxiv. p. 131, &c.

therefore, the combustion was carried on slowly, water might be formed, without the smallest portion of acid, even though nitrogen were present. This was the case, for example, in Mr Cavendish's experiment, in which atmospheric air was used. Nay, what appears at first view very singular, and contrary to the cause assigned, water formed by burning hydrogen in atmospheric air, is generally free from acidity ; while it is acid, when formed by burning hydrogen in oxygen. The reason assigned for this is, that in atmospheric air, the temperature produced by the combustion is not sufficiently high to cause the combination of the oxygen and nitrogen, while in oxygen gas, the heat produced at the point where the combustion proceeds is more intense, and any nitrogen present is brought into combination.

Another circumstance, having some influence in the production of this acid, was the proportion of the gases. If they were mixed in due proportion, so that no more oxygen was present than what is necessary to saturate the hydrogen, the water formed had no acidity ; but if the oxygen were in larger quantity, a portion of acid was always formed ;—the excess of oxygen combining with the small quantity of nitrogen present ; while, when there was no excess of oxygen, no combination of any portion of it with nitrogen took place, both as the hydrogen has a stronger attraction to oxygen, and as it combines with it with more facility. On this principle is explained an objection stated by Dr Priestley to this explanation. The presence of the nitric acid, in this case, he says, cannot be owing to a small portion of nitrogen having been present in the mixture of the gases inflamed ; for when a quantity of nitrogen is purposely added, the quantity of nitrous acid is not increased. But this might easily happen, if there were as much hydrogen present as was sufficient to saturate the oxygen, as any quantity of nitrogen which had been added would remain uncombined.

In some cases the acid was found to be not the nitric, but the carbonic: the origin of it was equally traced. The metals which are employed to decompose water to obtain hydrogen, zinc, and especially iron, generally contain a portion of carbon, a quantity of which is dissolved by the hydrogen as it is evolved, and this, when the hydrogen gas was burned, combined with a portion of the oxygen, and formed carbonic acid.

When care is taken to obtain the gases free from these impurities, or, by the manner of conducting the experiment, to prevent their combination with the oxygen during the combustion, the water is obtained perfectly free from acidity, or from any other impregnation, and its weight is equal to the weight of the oxygen and hydrogen combined. This latter fact has indeed been called in question; but it has been established by very accurate experiments on a large scale,—experiments which appeared to obviate every objection, and leave no doubt as to the composition of water.

The first experiment of this kind, in which a large quantity of the gases were combined with an accurate attention to the proportions, was made by Monge, in 1783. The oxygen was procured from the red oxide of mercury prepared by nitric acid, the hydrogen from iron-wire and sulphuric acid diluted with water. By repeated explosions in a close vessel, of a mixture of the two gases duely proportioned, 145 pints of hydrogen and 74 pints of oxygen were consumed; weighing, according to his estimate, 3 ounces 6 gros 27.56 grains. The product of water was 3 ounces 2 gros 45.1 grains. There was a residuum of air in the vessel, which weighed 2 gros 27.91 grains; on the whole quantity, therefore, there was a *deficit* of 1 gros 26.55 grains, which Monge accounted for from the imperfect manner in which he had made allowance for variations of barometrical pressure in estimating the volumes of the gases consumed in the progress of the experiment, and still more from no allowance having been made for changes of temperature in the vessels containing the gases contiguous to the balloon in which the explosions were made. The water obtained was slightly acid *.

La Fevre de Gineau, in 1788, made the experiment publicly on a very large scale. The oxygen was extracted from the black oxide of manganese by heat, the hydrogen was obtained from forged iron and sulphuric acid diluted with water. The volume of oxygen gas employed amounted to 35085.1 cubic inches, its weight to 254 gros 10.5 grains; the volume of hydrogen gas was 74967.4 cubic inches, its weight 66 gros 4.3 grains. The whole, therefore, weighed 320 gros 14.8 grains. The gases, however, being not perfectly pure, there remained uncombined a quantity of air, consisting of oxygen, nitrogen and carbonic acid, which weighed 39 gros 23 grains. The real quantity of gases, therefore, combined together, was 280 gros 63.8 grains, or 2 pounds 3 ounces 63.8 grains;

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* Mémoires de l'Acad. des Sciences, 1783, p. 78.

the water produced weighed 2 pounds 3 ounces 33 grains. On so large a quantity, therefore, there was a deficit only of 30.8 grains; and, considering the difficulty of estimating with perfect accuracy the weight of the gases, this may be regarded as a near approximation. The water was sensibly acid from the presence of nitric acid *.

But the most accurate experiment made by the French Chemists, was one by Fourcroy, Vauquelin and Seguin, in which the most scrupulous attention appears to have been paid, to obviate every source of error. The oxygen was procured from the decomposition of oxymuriate of potassa, by heat, the hydrogen gas from zinc, and sulphuric acid diluted with water. The combustion was carried on as slowly as possible, that any small portion of nitrogen present might not be combined with oxygen. The experiment continued 185 hours without interruption. The quantity of hydrogen employed amounted to 25980.563 cubic inches; of oxygen, 13475.198. There remained in the balloon a quantity of gas, which amounted to 987 cubic inches, and which on examination was found to consist of nitrogen gas 467, carbonic acid gas 39, oxygen gas 465, and hydrogen gas 16. After making due correction for the quantity of hydrogen gas which remained after the combustion, and for the quantity of carbon contained in the hydrogen gas that was consumed, and which had formed carbonic acid, and after making a similar correction for the quantity of oxygen which remained, and for the quantity of it that had been spent in the formation of

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* Journal de Physique, tom. xxxiii. p. 460.

carbonic acid, it appeared that there had entered into combination, so as to form water,

	Cubic inches.		Grains.
Hydrogen gas,	25963.563,	weighing	1039.358
Oxygen gas,	12570.942,	———	6209.869
The total weight of gases, therefore, was			7249.227
The quantity of water produced was found to be - - -			7245
The deficit, therefore, amounted only to			4.227

The water obtained was examined by Lavoisier, Brisson, Meusnier and La Place; it shewed no sign of acidity, not reddening in the slightest manner paper tinged, with the infusion of violets or of mallow; with nitrate of lime, it formed no precipitation, nor cloudiness: its specific gravity was to that of distilled water as 18671 to 18670 *.

The last experiment which I shall give on this important subject, is one made by Dr Higgins, before a philosophical society in London, with an apparatus more simple, but sufficient to give an accurate result: 416.5 grains of oxygen gas, and 72.5 grains of hydrogen gas were consumed, the weight of both being of course 489. The water produced, which was perfectly pure and free from all acidity, weighed 487 grains †.

These experiments appear sufficient to establish the conclusion, that water is a compound of oxygen and hydrogen. In some of them it was obtained perfectly pure; was the only sensible product; and corresponded in weight, as exactly as could possibly be expected from ex-

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* Mémoires de l'Acad. des Sciences, 1790, p. 485.

† Minutes of a Philosophical Society, p. 194.

periments in which gases are weighed, to the weight of the hydrogen and oxygen which disappeared. This coincidence of weight, and absence of all other sensible product, are sufficient to refute the opinion at one time maintained, that the water is merely that which pre-existed in solution in the gases, and had been deposited during their combination.

These experiments by synthesis have been likewise confirmed by analysis. This was effected by Lavoisier and Meusnier. It had been observed by Bergman, that when iron-filings are moistened with water, they are oxidized, and a quantity of hydrogen gas is collected. The nature of this experiment was now understood, the iron attracting the oxygen of the water, and the hydrogen assuming the elastic form. These chemists supposed that this action would be more rapid at a high temperature. They accordingly succeeded in decomposing water, by passing it through an iron tube, red hot, or through a tube of copper with a spiral piece of iron inclosed, at the same temperature; hydrogen gas was disengaged in considerable quantity, and the iron increased in weight, and had lost nearly its magnetic property *. The experiment was afterwards made by Le Fevre de Gineau with more accuracy, so as to prove that the quantity of hydrogen collected, added to the increase of weight which the iron gains, is equal to the quantity of water that disappears, or at least as nearly so as the nature of the experiment will permit the estimate to be made with accuracy †. According to

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* Mémoires de l'Acad. 1781, p. 269.

† Journal de Physique, tom. xxxiii. p. 464.

a subsequent statement by Lavoisier, when a coated glass tube is employed in this experiment, and soft iron wire rolled spirally placed within it, on transmitting through the red hot tube, the vapour of water from a retort connected with it, in which a measured quantity of water is kept boiling, when 100 grains of this water disappear, or are decomposed, the iron in the tube increases in weight, 85 grains, and 416 cubic inches of hydrogen gas, weighing 15 grains, are obtained *. A similar decomposition takes place, but with results rather more complicated, by transmitting water over red hot charcoal; the oxygen of the water combining with one portion of the charcoal, and the hydrogen dissolving another portion, and two compound gases being thus formed. They can be separated from each other, however, their quantities measured, and their composition determined.

Even at a low temperature, some of the metals, especially iron and zinc, decompose water with rapidity when their action is aided by that of an acid. This is indeed the common process for obtaining hydrogen gas, sulphuric acid being diluted with 6 or 7 times, muriatic acid with 4 or 5 times, its weight of water, and poured on zinc in small pieces, or on iron-filings or wire. That the acid merely promotes the decomposition of the water by the agency it exerts, probably by the affinity it exerts to the iron and the oxygen, and does not afford hydrogen immediately, is proved by the fact that it remains in the fluid undecomposed, being able to saturate just as much of an alkali as it would have done in its pure state; and

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* Elements of Chemistry, p. 140.

that the metal receives oxygen, is proved by its being found in the liquid, increased in weight, and in an oxidated state. This has frequently been made the subject of experiment, and was ascertained with much accuracy by Dr Fordyce; a given weight, 1000 grains of diluted sulphuric acid, being saturated with a solution of potassa, and the quantity of sulphate of potassa formed being obtained by evaporation, amounting to 978 grains. The same quantity of the same acid was employed to dissolve zinc, and, on adding to the solution, solution of potassa, so as to precipitate the metallic oxide, the liquid, together with the quantity of water employed to wash the precipitate, afforded by evaporation a solid substance, weighing 7 grains more than the sulphate of potassa in the former experiment. On re-dissolving it in water, a little of a yellowish powder separated, and by evaporation sulphate of potassa was obtained, weighing 976$\frac{1}{10}$ grains, nearly two grains less; a difference so inconsiderable as obviously to have arisen from the accidental loss which must more or less attend such experiments. 164 grains of zinc had been dissolved; the oxide, after being dried by a red heat, weighed 220 grains; the metal therefore had gained weight equal to 56 grains, which, from the preceding experiment, must have been derived from the oxygen of the water. And, by a subsequent experiment, Dr Fordyce shewed that a quantity of water equivalent to this disappeared during the solution *.

From the synthesis and analysis of water, by the experiments now described, the proportions of its constituent

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* Philosophical Transactions, 1792, p. 374.

principles have been determined. They vary a little, as inferred from different experiments.

	Hydrogen.	Oxygen.
Lavoisier stated the proportions at	15	85
Le Fevre de Gineau, from the analysis of water, at -	15.7364	84.2636
From the formation of water, in the experiment which has been related, he states them at -	15.2	84.8
From its formation in another experiment, he states them at	15.0406	84.9594
According to Fourcroy and Vauquelin, they are - -	14.338	85.662

They may with sufficient accuracy be fixed at the round numbers of 15 hydrogen, and 85 oxygen in 100 parts, this being very nearly the average of the above results, and, to any calculation which pretends to more accuracy, objections might be made.

Water has been decomposed, likewise, by the agency of electricity, so as to afford similar results. The experiment was first made by Troostwyk and Deiman, assisted by Mr Cuthbertson. The apparatus they used consisted of a glass tube, one-eighth of an inch in diameter, and 12 inches long, in one extremity of which was fixed, by melting the glass around it, a wire of gold 1½ inch long, this extremity of the tube being thus hermetically sealed. Another wire of gold or platina was introduced at the open end, of such a length as to be distant from the extremity of the other five-eighths of an inch. The tube thus prepared was filled with distilled water, freed of its air by the air-pump, and inverted in quicksilver. The wire at the top or sealed end was in contact with an insulated brass ball, placed at a little distance from the prime conductor of the electrical machine. The other wire communicated by a chain with the external coated surface of a Leyden jar, the ball of which was in contact with the prime conductor. On working the machine, the jar from this arrangement discharged itself, the electrical discharge being transmitted through the water. At each discharge, small air-bubbles were formed, and rose to the top of the tube; this continued until the water was depressed nearly to the lower extremity of the upper wire, and then a discharge occasioned the whole of the gas collected to disappear, a very small portion excepted. These chemists concluded, that by the agency of electricity the water is resolved into its elements, oxygen and hydrogen, and that when these accumulate sufficiently to permit the discharge to be transmitted through them, they are again combined and form water *.

This experiment has been rendered more satisfactory and more easy of execution by Dr Pearson. The general results were similar, gas being formed at each discharge, and this when accumulated sufficiently, being inflamed and made to disappear. A small portion of residual gas was always obtained. When common spring water had been used, this amounted, after 1600 discharges, when a column of gas, two-thirds of an inch in length, and one-ninth of an inch wide, was obtained, to one-third of the bulk of the gas. When the water was previously freed from air, by long boiling, or by the air-pump, the residual air after

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* Journal de Physique, t. xxxv. p. 369.

the explosion was not more than 1 part in 20, and this was no doubt a portion of atmospheric air, or of nitrogen, which the water had retained, and the electrical discharge had expelled. By removing the residual air after each explosion, without changing the portion of water in the tube, this would have been at length got rid of; but Dr Pearson could never carry the experiment so far, " the tubes being always broken after obtaining a few products, long before it could reasonably be supposed the whole of the air of the water was expelled from it." In some of these experiments, instead of exploding the air in the upper part of the tube, it was removed, nitrous gas was added, which proved the presence of oxygen by the appearance of red fumes, and a diminution of volume nearly of one-third. On adding pure oxygen to the remainder, and passing the electric spark through it, it was instantly diminished one-fourth. There can be no doubt, therefore, that in these experiments water was resolved into oxygen and hydrogen gases, and again formed by their combination; and as Dr Pearson has remarked, the evidence they afford in proof of the composition of water is peculiar, as in preceding experiments, by which water was decomposed, other substances were necessarily introduced, while in these water is the only ponderable substance concerned. The agency of electricity in producing these effects, is no doubt to be ascribed to the momentary high temperature it produces at the point at which it issues from or enters into the wire; when it issues it is momentarily accumulated from the comparatively imperfect conducting power of the water, and when it enters it is condensed by the superior conducting power of the metal [*].

It is a proof of the imperfection of the evidence on which chemical reasoning rests, that the conclusion with regard to the composition of water which appears to be so strictly deduced both from analytic and synthetic experiments, is still capable of being controverted, and a different view of the relation of oxygen, hydrogen, and water, maintained. This view has been suggested by the nature of the changes which water suffers when submitted to the action of galvanism; and as this presents some very peculiar phenomena, it will be necessary to consider it more fully.

When two wires from the opposite extremities of a galvanic battery are placed in a tube containing water, so that they are distant from each other $\frac{1}{4}$ or $\frac{1}{2}$ inch, or even more, a stream of gas issues from each wire, and continues as long as the connection is kept up, and the galvanic arrangement is in a state of sufficient power [†]. On examination, the gas from the one wire, that in the positive electrical state, is oxygen gas; that from the other, which is in the negative state, is hydrogen gas,—these are in the proportions which form water, and when exploded, either by the galvanic or electric spark, disappear. In order to avoid every source of fallacy from the presence of foreign matter, or from the chemical action of the instruments employed, it is necessary to use in the experiment distilled water, and to employ wires of metals not oxidable as those of platina or gold.

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[*] Philosophical Transactions, 1797, p. 142.

[†] The apparatus, Fig. 60. is generally used for this purpose; a slip of copper connected with the one extremity of the trough being placed on the brass cape *a*, fixed on the top of the glass tube, a wire of gold or platina being attached to the brass, and descending within the tube. The tube is placed in a brass cup *b*, the stalk of which is connected with the other extremity of the trough, and from which another wire rises into the tube. The tube being filled with water and inverted in the cup containing water, on establishing the galvanic connection, the de-

The nature of this decomposition of water by galvanism, obviously presents a considerable difficulty. We can conceive, that the galvanic discharge, when it issues from the wire, or enters into it, may, by the high temperature it excites, or by some other agency, decompose the particle of water at the extremity of the wire, separating the oxygen and hydrogen of which it consists, which might then assume the gaseous form. But we find by experiment that this is not the nature of the decomposition; the oxygen and hydrogen gases are not disengaged together, at each or either wire, but from the one wire, that connected with the more oxidable metal, or the plus side, oxygen escapes, and hydrogen from the other. If these are derived from the decomposition of water, the question is to be solved, What becomes of the hydrogen at the point at which the oxygen appears, or of the oxygen at that where the hydrogen is evolved?

The decomposition of water by galvanism was first observed by Messrs Nicholson and Carlisle *, and by these

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composition and the production of gas from each wire commence.

* Nicholson's Journal, 4to, vol. iv. p. 182.

philosophers also was observed the singular mode in which the decomposition takes place; they obtained even the gases separate, by inserting the wires into separate tubes; Mr Cruickshank and Mr Davy ascertained that the oxygen and hydrogen thus obtained are nearly pure, each of them being mixed only with a little nitrogen, derived probably from the atmospheric air of the water, and that they are obtained in the proportions which form water, so as to disappear when exploded *. It has been already stated, that the decomposition takes place with more or less rapidity as the wires are at a greater or less distance from each other. When distant only an inch in a tube $\frac{2}{10}$ inch wide, the disengagement of gas is rapid; it takes place at the distance of 5, 6, 8, or even more inches, if the galvanic battery is powerful. It is effected even when the wires are placed in different tubes, provided a communication be established between the water in these tubes by a galvanic conductor, as, if they be suspended in the same vessel of water, as represented in the apparatus Fig. 63. each wire being connected with one extremity of the galvanic battery. The same result is obtained if a portion of sulphuric acid be interposed between the two portions of water; and even as Ritter has affirmed †, if they are suspended in different vessels of water, provided a communication be established between them by a metallic arc, though in this case the production of gas is less copious; and even the separate evolution of the two gases is said to be less complete.

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* Nicholson's Journal, 4to, vol. iv. p. 255. 276.

† Ibid. p. 512.

Dr Wollaston thought of imitating the galvanic decomposition of water by applying electricity in a state approaching to that in which galvanism exists,—a stream of great tenuity moving with great velocity. Electricity was transmitted through very fine gold wires, fixed in a capillary glass tube, and the experiment so far succeeded that currents of gas arose from the wires; but in whatever way it was tried, the gases were not given out separately as in the galvanic arrangement, but each wire gave both gases [*]. Mr Davy, however, by carefully avoiding sparks, succeeded in obtaining the two gases in a separate state [†].

Different hypotheses have been proposed to explain this very singular decomposition of water by galvanism, or rather to account for the evolution of the two gases at different wires. It has been remarked, that there are but three ways of explaining the fact. "Either the galvanic action tends to abstract in each of the portions of water one of its constituent parts, leaving an excess of the other constituent part; or it decomposes the water, and permitting the disengagement of one of the gases at the extremity of one of the wires, conducts the other in an invisible manner to the extremity of the other wire, to allow it to disengage itself there; or, lastly, the water is not decomposed at all, but produces by its combination with a principle of some kind, proceeding from the positive side of the pile, oxygen gas; and by its combination with a principle issuing from the negative side of the pile, hydrogen gas [‡]."

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[*] Philosophical Transactions, 1803.

[†] Ibid. 1807.

[‡] Report to the French National Institute, quoted in Wilkinson's Elements of Galvanism, vol. ii. p. 150.

The first of these hypotheses was proposed by Monge, and appears to be adopted by Berthollet. In conformity to it, it must be supposed, that water, in common with many other compounds, can receive into its composition an additional proportion of either of its elements; that at the point, therefore, where hydrogen is given out when it is submitted to galvanic action, it remains with an excess of oxygen; and at that where oxygen is emitted, it must have an excess of hydrogen. The obvious objection to this hypothesis is, that by such changes in the proportions of its elements, the water ought to suffer a change in its properties. Where both wires were in the same space, this might not be perceptible, as the one portion mingled with the other might re-establish the original proportion as quickly as the galvanism subverted it; but where the portions of water are in separate tubes, this difference should soon be conspicuous. Such an action, too, must soon have a limit; while it appears to be sufficiently established, that a given portion of water may be entirely decomposed.

It appeared at one time, however, what is in conformity to this view, that besides the evolution of the gases at the different wires, certain other products are actually formed. It was observed even at an early period of these researches, that the water in which the positive wire was immersed, became sensibly acid, and the other portion, in which was the negative wire, became alkaline. Mr Cruickshank explained this, from the portion of atmospheric air which water holds in solution; the oxygen evolved at the positive wire combining in its nascent state with the nitrogen of this air, and forming nitric acid; the hydrogen evolved at the negative wire combining with the nitrogen of the air, dissolved in the water in which it is immersed, and forming ammonia. It afterwards appeared, however, from some experiments, that the acid produced at the positive side is muriatic acid, and that the alkali at the negative side is a fixed one, either potassa or soda. The production of the muriatic acid was observed by Pacchioni of Pisa, by Brugnatelli, and by other chemists; and the production both of this acid and of a fixed alkali were observed by Mr Sylvester, when the experiment of the decomposition of water was performed by placing galvanic wires in separate vessels. Whence he concluded, that muriatic acid is water *plus* oxygen, and the alkali water *plus* hydrogen *.

It has since been clearly shewn, that this apparent production of muriatic acid and fixed alkalis is owing either to impurity of the water, or to the vessels being acted on in which the experiment is made. The Galvanic Society of Paris repeating Pacchioni's experiment, and avoiding these sources of fallacy, could discover no trace of muriatic acid in the decomposed water †. The same result was obtained by Pfaff ‡. Mr Davy, by establishing the law which regulates the decomposition of chemical compounds by galvanism, and shewing more clearly the force with which certain principles are attracted to each galvanic pole, proved, that if the smallest quantity either of acid or of alkali be present in the water,—a quantity not capable even of being detected by re-agents, the one is attracted to the one side, the other to the other; and also, that the containing vessels, if they have any portion of these, yield them to the galvanic force; glass vessels, for example, furnishing soda. A little nitric acid too, and ammonia, are liable to be formed from the influence of the air, as Cruickshank had explained. One or other of these Mr Davy proved, by an extensive series of experiments, is the source of the acid and of the alkali that appear to be produced; when these are avoided, the water to the end of its decomposition remains pure, "and water chemically pure is decomposed by electricity into gaseous matter alone, into oxygen and hydrogen *." The hypothesis of Monge, which derived support, therefore, from these supposed facts, cannot be maintained.

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* Philosophical Magazine, vol. xxiv. p. 176. vol. xxviii. p. 55. 59. Nicholson's Journal, vol. xv. p. 50.

† Philosophical Magazine, vol. xxiv. p. 172.

‡ Ibid. vol. xxix. p. 19.

The second hypothesis to account for the phenomena of the decomposition of water by galvanism,—that a particle of water is decomposed, and its oxygen conveyed by the galvanic influence to the one wire, and allowed to escape, its hydrogen to the other, was proposed at an early period by Cruickshank, and afterwards modified by Bostock, Vauquelin, and Thenard; the galvanic fluid being supposed, in Cruickshank's explanation, to combine with the oxygen of the water, and to convey it in this combined state to the opposite pole, where it allowed it to escape, or, according to that of the other chemists, to combine with the hydrogen, and convey it in a similar manner†.

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* Philosophical Transactions, 1807.

† Nicholson's Journal, 4to, vol. iv. p. 257. Ibid. 8vo, vol. iii. p. 9. 74.

The explanation which Mr Davy gave of this decomposition, in conformity to the general law which he established as regulating all the decompositions which galvanism produces, may be regarded as a modification of this hypothesis, not embarrassed by the improbable assumption of galvanism entering into combination with either of the elements of water. The general law has been already stated, (vol. i. p. 551.), and also its application to this particular case. The law is, that different substances have such a relation to galvanism, that some are attracted forcibly to the positive, others to the negative side of the galvanic arrangement; oxygen and those compounds in which it predominates being attracted to the positive side ; hydrogen, inflammable and metallic substances, to the negative. Hence, when water is submitted to the action of galvanism, the oxygen of a portion of it is attracted to the positive side, and its hydrogen repelled : the opposite process takes place at the negative side, the hydrogen being attracted, and the oxygen repelled ; and at the wires connected with the two sides, these gases appear in their insulated form. The general law, though presenting very singular results, being established by very ample experimental evidence, in which this separation of the constituent principles of bodies, and conveyance of ponderable matter to a distance are demonstrated, the application of it to the decomposition of water appears necessarily to follow, and to preclude any other hypothesis.

The recent speculations of Mr Davy, however, appear to lead to a different explanation, more analogous to the third hypothesis, and involving even the conclusion, that water is not a compound body, but is the ponderable base, both of oxygen and hydrogen gases, assuming these forms according to its electrical states. An hypothesis of this nature had been advanced by Ritter, and adopted by some of the German and British Chemists. Water they regarded as simple; when united to positive electricity it constitutes oxygen gas; when united to negative electricity, it forms hydrogen gas, and in both is the sole gravitating matter. Hence are explained the phenomena presented in the action of galvanism on water,—the water at one wire receiving positive electricity, and appearing as oxygen, and at the other receiving negative electricity, so as to assume the form of hydrogen. This hypothesis appeared so extravagant and chimerical, that little attention was paid to it by chemists. It is now brought forward, however, by Mr Davy, as connected with the general theory of the dependence of the chemical forms of matter on electrical powers. According to this theory, water "must be supposed a constituent part of all the different gases; but its electricities in oxygen and hydrogen would probably be the very reverse of what they have been supposed by Mr Ritter and some ingenious English inquirers. Water positively electrified would be hydrogen; water negatively electrified, oxygen: and, as in the physical experiments of temperature, ice, added to certain quantities of steam, by an equilibrium of heat, produces water; so in the chemical experiment of the generation of water, the positive and negative electricity of oxygen and hydrogen in certain proportions would annihilate each other, and water alone be the result *."

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* Philosophical Transactions, 1808.

This hypothesis receives perhaps some confirmation from the farther discovery of the relation between nitrogen, and hydrogen, and oxygen, which has been already pointed out; at least, Mr Davy is disposed, from these facts, to consider the general theory, that the different forms and properties of these substances depend on their electrical state, as the most probable one. It is obvious, however, that the investigation of this subject is not sufficiently advanced to admit of any certain conclusion with regard to it; and it would be of little utility to engage in a discussion, of what will probably soon be determined by the progress of discovery.

In the combination of oxygen and hydrogen, (if this language is still to be employed, and water is to be regarded as formed by such a combination), there are presented the singularities of the combination taking place only in one proportion, and of the compound having no acid powers. The properties, therefore, of these principles, are mutually neutralized; or the combination, according to the view which Berthollet gives, is somewhat analogous to that in a neutral salt, in which the reciprocal affinity exerts the greatest effect, and the opposing properties of the ingredients have become equally latent. If the hydrogen predominated in water, the compound might be expected to have inflammability, as we observe this property in nearly all the combinations into which hydrogen enters. If the oxygen predominated, it would have acidity, as this quality appears always to arise from the predominance of oxygen. The degree of condensation attending the combination is very great, the volume of the elements being reduced in water to $\frac{1}{2000}$. From this condensation and perfect neutralization, may be supposed to arise the comparatively weak chemical action which the compound exerts.

Although water does not exert very energetic affinities, so as to combine intimately with bodies, and saturate their properties, still it is an important chemical agent, from combining with many substances, and, without much altering the order of their attractions, communicating that fluidity which is in general requisite to chemical action. Hence it is a common medium, in which many substances are brought to act on each other; and so little does it modify their mutual attractions, that it is seldom considered in the theory of the operations in which it is thus concerned.

Water is tasteless, colourless and inodorous. It owes its fluidity to the presence of caloric, its natural state, like that of other bodies, being solidity. It passes into this form at 32° of Fahrenheit, and then suffers a regular crystallization. This is seen very evidently in the slow congelation of water, lines shooting from the sides of the vessel, and from each other, at a certain angle, that of 60° or 120°, and not less evidently in the radiated appearance of a flake of snow. The figures of the crystals of ice, according to Hassenfratz [*], is that of a hexaedral prism; in hail, according to M. d'Antic, it has the form of an octaedron. By the continuance of the crystallization, the vacuities between the lines or crystals are filled up, and a solid brittle and transparent mass is formed, the state in which ice usually occurs. When caloric is communicated to ice or snow at 32°, fusion takes place, accompanied with an absorption of caloric, from an enlargement of capacity. There is, at the same time, a diminution of volume, water at 32° being more dense than ice at the same temperature. This diminution of volume continues to proceed, (as has been already fully stated), as the temperature is raised several degrees above 32°; and the greatest density of water appears to be about 40° of Fahrenheit. In receding from that temperature, either to a higher or lower, it expands in an increasing ratio, the expansion, as the temperature falls, continuing until it becomes solid, and in the very act of freezing it exerts a strong expansive power. A quantity of air which the water held dissolved is expelled, and hence the ice is porous; but the expansive force, and probably also the enlargement of volume, as it approaches the freezing point, is principally owing to the new arrangement into which the particles, from their polarity, appear to pass.

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[*] Journal de Physique, tom. xxxiii. p. 57.

Even at a temperature below 32°, ice passes into vapour when exposed to the atmosphere, undoubtedly from the affinity exerted towards it by the gases composing atmospheric air. Water likewise evaporates slowly at a low temperature; the evaporation becomes more copious as the temperature is raised; at 212° it boils, under the mean atmospheric pressure, or that which is equal to the pressure of 29½ inches of mercury, *in vacuo* at about 90° of Fahrenheit; and, in passing at any temperature into vapour, it absorbs a quantity of caloric, which becomes latent; this latent caloric, according to Mr Watt's observation, being less as the temperature of the water from which it is produced is greater; in other words, being less when produced under a greater pressure, than when produced under a less pressure *.

When the vapour of water, as steam, is fully formed, it is transparent and invisible; when condensing, a degree of opacity arises from the approximation of its particles. It occupies at 212°, according to Mr Watt, 1800 times the space which it does when in form of water, and appears to have a specific gravity to that of atmospheric air at the same temperature, as 10 to 14. The elastic force it exerts is increased by every elevation of temperature, and, according to Mr Dalton's experiments, nearly in geometrical progression. He has given a table of this force for a considerable range of temperature, founded partly on experiment, and partly on calculation, by interpolation, which may perhaps be regarded as an approximation to accuracy, and which has been already inserted, as well as the table, with results somewhat different, which has been given by Betancourt, (vol. i. p. 217, 218).

The elasticity of steam thus increasing at a high ratio, by elevation of temperature, it is a mechanical agent of great power, and is productive of immense force under the most complete controul and adaptation in the steam engine, one of the most perfect instruments of human invention.

By a sufficient reduction of temperature, or by subjecting it to sufficient pressure, steam returns to the state of water, and gives out its latent caloric.

Water is compressible, though to no great extent. This

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* Philosophical Transactions, vol. lxxiv. p. 335.

was proved by Mr Canton, by including it in a glass flask, with a long and narrow neck. When the pressure of the atmosphere was removed by the air-pump, it rose a little in the neck; when the pressure was augmented by the condenser, it fell.

Water is capable of absorbing every substance existing in the gaseous form, but in very different quantities, according to the affinity which it exerts towards them. Of some of the acid gases it absorbs many times its own bulk, while of other gases, the three simple ones, for example, the quantity absorbed is so inconsiderable, as to require an apparatus of some delicacy to measure it. This has been made the subject of experiment by Mr Henry; the results are given in the following table of the quantities of the following gases, absorbed by 100 measures of water, freed from air by previous boiling, at the temperature of 60°.

Nitric oxide gas, -	5 measures.
Oxygen, - - -	3.55
Phosphuretted hydrogen,	2.14
Gaseous oxide of carbon,	2.01
Carburetted hydrogen gas,	1.40
Nitrogen gas, - -	1.47
Hydrogen gas, - -	1.53 *.

The quantities absorbed are greater as the temperature is low, until the water freezes, when it parts with those gases to which it has not a strong affinity, while those to

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* Philosophical Transactions, 1803, p. 276.

which the attraction is stronger are retained. The absorption is also aided by pressure, as had been long known to chemists. Dr Henry made this, too, the subject of experiment, and states as the result, with regard at least to those gases which are absorbed in small quantity, the important general law, "That under equal circumstances of temperature, water takes up, in all cases, the same volume of condensed gas, as of gas under ordinary pressure." Hence, as the spaces occupied by every gas are inversely as the compressing force, it follows, "that water takes up, of gas condensed by one, two, or more additional atmospheres, a quantity which, ordinarily compressed, would be equal to twice, thrice, &c. the volume absorbed under the common pressure of the atmosphere." By increasing pressure, therefore, a very large quantity of any gas may be made to be absorbed by water; and by various mechanical contrivances, several chemical artists have succeeded in impregnating water strongly with the different aeriform fluids. Paul of Geneva has, in particular, combined by pressure, large quantities even of those gases which are very sparingly soluble in water. According to his statement, the water is made to absorb half its volume of oxygen gas, one-third its volume of hydrogen, and two-thirds of carburetted hydrogen. It is somewhat singular, as is mentioned in the Report to the National Institute, that the water impregnated with these gases acquires no new properties. It differs little from common water in taste, produces no effervescence on being uncorked, nor affords, by the test of re-agents, appearances which would indicate clearly the presence of the gas with which it had been impregnated. The small portion of gas which could be extracted was found to be that with which the water had been impregnated, tolerably pure *.

Mr Dalton has considered the absorption of gases, thus produced by pressure, as merely a mechanical effect; the gas by the pressure being forced into the interstices of the fluid, and existing in it, with its elasticity unimpaired, precisely as without. From the principle which has been already frequently stated, that, probably, all substances have mutual affinities, which external forces only prevent from being energetic, or even apparent, there is every reason to believe that the absorption of gases by water is a chemical effect, arising from the mutual affinity between the particles of the water and those of the aeriform fluid; and on such a principle the phenomena can be fully explained. The obstacle to this affinity is the elasticity of the gas; hence whatever represses it, as a reduction of temperature, or the application of pressure, must favour the mutual attraction, and increase the quantity of gas absorbed. In reducing the temperature, there is a slight counteracting circumstance, introduced from the increased cohesion which is at the same time communicated to the fluid; but in applying pressure, there is no effect of this kind; it operates simply in counteracting the elasticity of the gas; its effect therefore will be proportional to the extent to which it is applied; and the law discovered by Dr Henry is just as conformable to the one theory as it is to the other.

A very plain proof that this view is just, is, that the ef-

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* Report to the National Institute on Paul's Artificial Mineral Waters, p. 20.

fect of pressure is precisely similar in increasing the absorption of those gases, between which and water the existence of a chemical affinity cannot be denied, as muriatic acid gas. Since, in this case, the effect of pressure in increasing the quantity of gas absorbed by the operation of a chemical affinity, must be acknowledged, why should it not be admitted in the other? There is no difference but in the quantities absorbed from the different forces of affinity. In the one case are clearly exemplified the effect of elasticity as an antagonist to the mutual affinity, and the operation of pressure in diminishing it; and the same view is of course equally to be applied to those cases, where the absorption is less considerable from the mutual affinity being less strong. In reality, all must be explained on the same principle; for the difference in the quantity absorbed introduces no essential difference into the nature of the operation; and it would be easy, by making experiments on all the gases, to form a series of quantities absorbed, from that which is greatest to the least; so that it would be impossible to point out the line of distinction between those where the absorption might be conceived to be purely mechanical, and those where the exertion of affinity must be allowed to operate.

Mr Dalton has lately replied to this argument *, that "nothing is more easy than to point out the exact line of distinction: wherever water is found to diminish or destroy the elasticity of any gas, it is a chemical agent; wherever it does neither of these, it is a mechanical agent." I would ask Mr Dalton where is the proof that

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* System of Chemical Philosophy, p. 206.

in any case the elasticity of a gas absorbed by water remains? Carbonic acid, which he considers as mechanically absorbed by water, is, so far as we can discover, in the same state as muriatic acid, which he admits to be chemically combined. Remove pressure from the liquid, and both will in a great measure escape. The only difference is, that as the affinity of water to muriatic acid is stronger than to carbonic acid, more of the former is absorbed under a given prsssure; and for the same reason, when the pressure is removed, more of it will be retained; otherwise the two cases are precisely alike. It is inferred, indeed, by Mr Dalton, that they are different, but this is only an inference resting on the assumptions which constitute his theory; and to assume this inference as established, and give it as a proof of the theory, will perhaps be found to be little more than reasoning in a circle.

If the absorption is the effect of a chemical affinity, it must be expected, that even in those cases where the affinities are weak, they will differ in force, and hence different quantities will be absorbed. This the preceding table shews to be the fact; and it is one, which, while it follows from the above view, and is therefore a proof of it, is inconsistent with the hypothesis, that the absorption is purely mechanical, and that the particles of gas existing in the fluid still retain their elasticity unimpaired. If neither oxygen nor nitrogen have a chemical affinity to water, why should the one be absorbed in the proportion to 100 of 3.5; the other of only 1.5.

If the absorption in these cases be a mechanical effect, it ought to be the same in other fluids; while, if dependent on affinity, as this must be of various force, it may be expected to be different. Mr Dalton h stated, that most liquids free from viscidity, kohol, &c. appear to absorb the same quantit pure water. Of this, however, as a general posi is much reason to doubt, or rather, indeed, to -, that the reverse holds good. Mr Davy, for example, found, that nitrous oxide gas is absorbed in larger quantities by alkohol, or ether, and even, notwithstanding their viscidity, by essential and expressed oils, than by water *.

From the experimental researches of Mr Dalton and Dr Henry on the absorption of gases by water, several important facts with regard to it, independent of all theory, have been established. Thus, if water be agitated with a mixture of two or more gases, portions of both will always be absorbed, the same as if they were presented to it separately in their proper density; the quantity therefore being greatest of that which separately is most largely absorbed by water. Or, if water has been previously impregnated with one gas, on agitating it with another, a portion of the latter will be absorbed, and a portion of the former displaced. This fact had been long known. It had been remarked by Dr Brownrig, as Dr Henry observes, in the example of the mineral waters impregnated with carbonic acid, from which the gas escaped when they were exposed to the air; while, when excluded from the air, although liberty was given for the gas rising into an empty bladder, the gas did not spontaneously separate. Hence, as water, unless submitted to certain operations, contains a portion of atmospheric air, in agitating any pure

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* Chemical Researches, p. 240.

gas with it, while a quantity of this is absorbed, a portion of the air the water held dissolved will be separated, and added to the residual gas, whence frequently sources of error have arisen in chemical experiments; and even in transmitting a gas through water, a small degree of admixture must, from the same cause, take place. This effect on the chemical theory, must be ascribed to the affinity of the one gas to the water weakening the affinity of the water to the other.

From this last fact, the relation of water to atmospheric air may be in some measure understood. If agitated with it, a portion is absorbed; but the two chief constituent gases of the atmosphere, the oxygen and nitrogen, are not equally affected, the former being absorbed in preference to the latter. This was long ago observed by Scheele; he found, that when atmospheric air was confined in a vessel with water that had been boiled to free it from air, it diminished in volume, and the residual air was at length incapable of supporting combustion *. Priestley observed, too, that water agitated with atmospheric air, absorbed the oxygen in preference to the nitrogen. Berger has shewn, that by repeatedly transmitting atmospheric air through a column of water, it suffers this decomposition, and that thus the whole of its oxygen nearly is abstracted †. Sometimes, however, the presence of one gas in a water, causes a larger portion of another to be absorbed. Thus, the presence of oxygen favours the absorption of nitric oxide gas, and even of hydrogen, ac-

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* Experiments on Air and Fire, p. 164.

† Journal de Physique, tom. lvii. p. 1.

cording to the observation of De Marti[*]; this bei dently owing to the affinity of the one gas to the ot

Any aëriform fluid absorbed by water must, it is vious from the preceding facts, be most effectually retai ed in combination by the pressure of gas of its own kind.

A singular fact has been stated by Biot, on the authority of De Marti, with regard to the absorption of gases by water. If water be repeatedly agitated with an aëriform fluid, suppose oxygen in a phial, it will be saturated with it, and after the last agitation, on opening the phial under water, there will be no farther diminution. If the phial after this be accurately closed with a glass-stopper, and put aside for a few days, on then opening it under water, a portion will enter the phial, shewing that part of the gas had been absorbed. If this be repeated from time to time, a fresh quantity of gas will always be found to have been absorbed, and the effect will be more perceptible the longer the air has been exposed to the water in the phial[†]. If the fact be fairly established, it appears to prove that the combination is at first not perfect, but that it gradually becomes more intimate. This effect was observed not to take place with nitrogen gas.

All water which has been exposed to atmospheric air, as spring and river water, contains a portion of air, from which it derives a sparkling quality and agreeable taste. From Mr Henry's experiments, a considerable portion of this air appears to be carbonic acid. He found, that by long boiling, 100 cubic inches of spring water gave 4.76

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[*] Nicholson's Journal, vol. xviii. p. 125.

[†] Ibid. p. 124.

of gas, of which 3.38 were carbonic acid, and 1.38 atmospheric air *.

This air is expelled again from water with great difficulty. If pressure be removed by placing it in the exhausted receiver of the air-pump, part of it is disengaged; by strong boiling, a considerable portion of it also is expelled, and likewise by freezing. But a quantity is still retained, which is not expelled by any of these means. This was very apparent in Dr Pearson's experiment on the decomposition of water by electricity; although he endeavoured to free the water from air by boiling, and by the air-pump, yet a portion still remained, which was disengaged by the electric discharge, and mingled with the gases from the decomposition of the water. It appears, too, from the experiments of Priestley, air being extricated from water by boiling repeatedly, apparently without limit, though in very small quantities, the water in the intervals of boiling, cooling, and discharging the air, being confined over mercury so as not to come into contact with the atmosphere: the same continued, but in considerable production of air, he observed, by abstracting pressure from water confined over mercury in a barometer tube. The same result was obtained in the experiments already related (p. 37.) in the extrication of air from water by freezing, if the air which in these experiments did appear to be given out without any limit can be regarded as air which the water held loosely dissolved. According to Dr Priestley's observation, the first portion of air that is expelled from water, is purer than that of the atmos-

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* Philosophical Transactions for 1803, p. 39.

phere; the next less pure, and at last it is, as he terms it, wholly phlogisticated *.

The presence of oxygen loosely combined in water, which has thus been exposed to atmospheric air, Scheele supposed to be discovered by dissolving in it a small quantity of green sulphate of iron. If the water be entirely free of oxygen, and if the vessel be well stopt, the solution is transparent; but if otherwise, it becomes slightly turbid, from the oxide of iron attracting the oxygen, and a small portion of it in this more highly oxidated state leaving the acid and being precipitated. There is some reason to suspect, however, that the partial decomposition of the sulphate in this experiment is owing to the affinity of the water to the acid, increased by its quantity; and accordingly, it has been stated by Darso †, that the precipitate takes place equally in using common distilled water, and distilled water from which the air had been completely expelled. Another method has been pointed out by Driessen: the water is to be boiled for two hours in a flask filled with it, and immersed in a vessel of water kept boiling, with the mouth of the flask under the surface of the water; it is to be inverted in quicksilver, taking care that no air-bubble adheres to the side of the flask; and being tinged with infusion of litmus, a little nitrous gas is to be introduced; if the oxygen has been sufficiently expelled from the water, the purple colour of the litmus does not

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* Additional Experiments on the Generation of Air from Water, p. 22.

† Nicholson's Journal, vol. xvii. p. 275.

change; while, if oxygen be present, it immediately becomes red *.

From the difference in the affinities which water has to oxygen and to nitrogen gases, and from the fact that one gas exposed to water always displaces more or less of another, is explained,—a circumstance which has been the source of some fallacies, and which in experiments in pneumatic chemistry requires to be carefully attended to. If a quantity of oxygen gas be kept in a jar which is inverted and placed in water, the purity of it is diminished, a quantity of nitrogen gas is found to be mixed with it; and if it be kept long in this situation, the quantity of nitrogen will even be considerable. The water which is exposed to the atmosphere imbibes both oxygen and nitrogen; this nitrogen being retained by a weak affinity, the pure oxygen in the jar, by the superior attraction which exists between it and water, detaches it, and it mingles with the remaining oxygen gas, and contaminates its purity. Hydrogen gas is affected in a similar manner, nitrogen mixing with it when it is kept long over water which is in contact with the atmosphere; and all gases, in such a situation, become impure.

Water which has descended slowly through the atmosphere may be expected to be saturated with oxygen, and accordingly it is affirmed that dew, rain-water, and snow, contain more oxygen loosely combined than water does in its usual state. This has been in particular maintained by Hassenfratz. Air drawn from rain-water, he affirms, suffers a diminution of volume by exposure to phospho-

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* Philosophical Magazine, vol. xv. p. 252.

rus, equal to 35 in 100; while air drawn from the water of the Seine gave a diminution of only 20. To prove the presence of oxygen in snow, he gives the following experiment: 1000 grammes of snow were put into one jar, and 1000 grammes of distilled water in another; into each of them was poured an equal quantity of the same infusion of turnsol; both were placed in a warm temperature; and after the snow melted, he remarked, that the dye of the snow-water was deeper than that of the other. The experiment was repeated with sulphate of iron. To 1000 grammes of snow, and 1000 of distilled water in separate jars, were added pure and clean sulphate of iron, 6.5 grammes to each. In the first, the precipitate of oxide of iron amounted to 0.150 grammes, and in the other only to 0.010 *. Admitting the accuracy of the experiment, it is inconclusive, at least in proving that snow contains more oxygen than water which has been exposed to the air, as the comparison was instituted, not with water in this state, but with distilled water. Carradori has endeavoured to shew, that snow-water is even quite destitute of that loosely combined oxygen which is present in common water, fishes put into it dying much sooner than they do in common water, when the renewal of air is equally prevented in both cases by a layer of oil on the surface of the water; but when the snow-water has been exposed for some time to the air, the fish are capable of living in it much longer. He adds, that snow-water exposed to the action of light does not give out oxygen †. Admitting

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* Philosophical Magazine, vol. iii. p. 237—38.

† Journal de Physique, t. xlviii. p. 226.

also these facts, they are not perhaps perfectly conclusive. The opinion of Hassenfratz, on the other hand, appears to have originated from hypothetical views, principally from the supposed fertilizing quality of snow; and the experiments he adduces are not sufficient to establish the conclusion which he draws, that the oxygen in snow is in an intimate state of combination. Bergman long ago remarked, that although snow-water affords some traces of nitrous acid, it is when newly melted totally void of air *. And from an experiment made by Saussure on the air from the interstices of snow, it appeared to be even less pure than atmospheric air †.

Some striking experiments connected with this subject, and leading to important results as to the nature of water and ice, were made by Ritter, of which Professor Jameson has favoured me with the following abstract. Ritter having had his attention directed to the freezing of water under the influence of galvanism, found, as he affirms, that the portion in contact with the *minus* side of the pile, freezes sooner than that at the *plus* side, which he ascribed to a difference in the composition of the water; that in the former situation being supposed to have an excess of hydrogen; that in the latter an excess of oxygen. This led him to attend more particularly to the fact which had been long known,—that air-bubbles are disengaged from water in freezing. These could never be well collected, so as to be submitted in any quantity to accurate examination, as they are entangled in the interstices of the ice, and are absorbed again when it is melted. He therefore endeavoured to discover the nature of this aëriform fluid, by mixing certain re-agents with the water designed to be frozen.

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* Essays, vol. i. p. 114.

† Voyages, t. vii. p. 472.

He first mixed a quantity of concentrated colourless muriatic acid with water, which he divided into four portions. Into each a stripe of gold-leaf was suspended; two of them were exposed to an intense cold; the water was frozen, while the acid remained liquid beneath; the ice had few air-bubbles. These vessels were now exposed to a temperature sufficient to melt the ice; the slips of gold-leaf were examined; the part which had been towards the surface of the liquid was unaltered, while that beneath was corroded; and the liquid, when subjected to the action of muriate of tin, gave the colour and cloudiness which is produced by a solution of gold. The gold-leaf in the two portions of diluted acid, which had not been frozen, remained unaltered, and gave no colour or precipitate with the muriate of tin. Hence Ritter concluded that oxygen had separated from the water in freezing, and had combined with the muriatic acid, converting it into oxymuriatic acid, which had dissolved a portion of the gold.

In suspending oxide of iron in water subjected to cold, so as to freeze it, he found the oxide to become of a yellow or red colour, as it does when it receives more oxygen. But the most beautiful, and apparently the most decisive experiment, was diffusing in portions of water a quantity of newly prepared white prussiate of iron, (a substance, which by the blue colour it assumes, when it receives oxygen, is a very delicate test of that principle), excluding the action of the air by a thin layer of oil on the surface of the liquid. These vessels were exposed to unequal degrees of cold, and as often as any portion froze, the white precipitate became blue.

These experiments prove, that oxygen is separated during the congelation of water, and hence Ritter concludes, that ice contains an excess of hydrogen, and by some subsequent experiments has endeavoured to shew, by the blackening of muriate of silver, exposed to melting ice, that it gives out hydrogen in passing to the state of water. The experiments would require to be repeated; and from the first series, at least, it would perhaps still remain doubtful, whether the effects were not owing to the separation of the oxygen not essential to the composition of water, but held by it in a state of solution, the last portions of it being retained with much force, and being disengaged by the freezing. They are at variance, too, with the experiments of Priestley already related, which prove, that the air extricated from water in freezing is nitrogen.

Water is contained in all the gases, derived either from the materials from which they have been extricated, or from the water through which they are transmitted. This appears to exist in them in vapour, in a state of loose combination, is capable of being discovered by the various hygrometrical substances, and may be abstracted by exposing the gas to such bodies as have a strong attraction to water, as lime, or muriate of lime. The existence of water in this state in atmospheric air has been already considered, under the history of the atmosphere. But besides this, it has been supposed, that there is in elastic fluids, a portion of water in more intimate combination, and that this is even necessary to their existence in the elastic state. This is a question of considerable interest: but involving minute details, and being intimately connected with the investigation of the constitution of some compounds, the history of which remains to be given, I consider it preferable to place the discussion with regard to it in a note. Note E.

Water is the general solvent of saline substances. It dissolves the alkalis in large quantities, and likewise all the acids. The affinity of some of them to it is even so strong, that they cannot be obtained entirely free from it. The greater number of the neutral salts too are soluble in it, and when they crystallize retain a portion of it, as water of crystallization.

Water is likewise capable of dissolving the earths; some of them in considerable quantity, particularly barytes and strontites; the others more sparingly. Even those earths and stones which it cannot dissolve, it wears away and reduces to a state of extreme division, partly by attrition, and partly by its chemical powers. The remarkable power which it has of corroding and minutely dividing those earths which it cannot dissolve, gave rise even to an opinion that it was convertible into earth. It was observed by Boyle, that water when distilled even 200 times, deposited each time a quantity of earth, and was itself diminished in the progress of the experiment, observations which were confirmed by succeeding chemists. A more attentive examination shewed, that the origin of the earth was from the glass vessels employed in the operation, as these were found to be eroded and diminished in weight. A striking experiment in proof of this is given by Scheele, and which demonstrates the chemical action of water on glass, when it is aided by a high temperature. A quarter of an ounce of distilled snow-water was put into a small glass matrass, the neck of which was drawn out to the length of two feet, the water was boiled in it, and when the atmospheric air was expelled, the orifice was closed. It was suspended over a lamp, and the water kept continually boiling for twelve days and nights; after it had boiled two days it became white, after six days it was like milk, and at the end of the twelfth day was quite thick: on allowing it to remain at rest, a powder subsided, from which the water was poured off clear; it was sensibly alkaline, no doubt from the alkali of the glass, and also held a portion of silex dissolved; the deposite was likewise siliceous earth. On breaking the matrass, the inside of it was dim and rough, as far as the boiling water had reached *. Lavoisier, by very accurate experiments, proved likewise, that this is the source of the earth, which appears when water is boiled or distilled in glass vessels †.

Water, though incapable of combining directly with the metals, exerts a chemical action upon them. At ignition it affords oxygen to several of them; and at a natural temperature, aided by atmospheric air, it oxidates or corrodes the greater number of them. At a high temperature it is also decomposed by charcoal and sulphur, which receive from it oxygen.

Water is a solvent of many other substances. Few of the animal or vegetable products are insoluble in it, and all of them are more or less affected by it as a chemical

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* Treatise on Air and Fire,—Preface.

† Mémoires de l'Acad. des Sciences, 1770, p. 397.

agent, receiving from it oxygen, or the re-action of their constituent principles being promoted by the fluidity it communicates.

From the extensive solvent power of water, it is scarcely ever met with pure in nature. Every kind of spring or river water is impregnated with saline and earthy bodies of different kinds, and in various quantities, according to the nature of the strata over which it has passed. Spring water contains, according to Bergman, a little carbonate of lime, muriate of lime, and muriate of soda; river water contains carbonate of lime, muriate of soda, and each of these also sometimes a little alkali *. Well-water, besides these, contains always a portion of sulphate of lime, the presence of which is the cause of the quality in waters termed *hardness*. Rain or snow water is freer from these foreign substances, but is still not perfectly pure. Rain water collected as pure as possible, and with every precaution, contains, according to Margraaf, muriate of soda †, and according to Bergman, muriate of lime. Water is freed from these substances by distillation; and for any chemical process in which accuracy is requisite, distilled water must be used.

When water is impregnated with foreign substances, so as to acquire peculiar taste or smell, or to suffer an obvious alteration in some of its other qualities, it is regarded as a mineral water.

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* Chemical Essays, vol. i. p. 192.

† Mémoires de l'Acad. des Sciences, 1770, p. 386.

BOOK III.

OF ALKALIS AND THEIR BASES.

AN order of substances, possessed of very important chemical properties, has long been distinguished by the title of ALKALIS. Their characters are extremely appropriate. They impress an acrid taste; inflame or erode the skin, and dissolve animal matter, a property which has been named Causticity: they have a strong attraction to water, and combine with it with rapidity and in large quantity: they change the blue and green colours of vegetables to a green, the yellow to a brown: they unite with oils and fats, forming soap: and they combine with the individuals of another class of chemical agents, the acids, and form compounds, in which, when the combination is established in certain proportions, the acid and alkaline properties are mutually neutralized. They are also capable of being fused and volatilized by heat. There are three alkalis. One of them from existing when uncombined in the gaseous form, has been named Volatile Alkali; to the other two the epithet Fixed has been given. In the modern nomenclature the volatile alkali has received the name of Ammonia; the others the names of Potash (or what ought to be preferred, for similarity of termination, Potassa) and Soda.

Alkalis are more particularly distinguished as chemical agents, by properties the reverse of those of the substances denominated Acids. These two classes are in some measure co-relative; the one are opposed to the other; and in entering into combination, the acids always diminish the alkaline properties: the alkalis are equally subversive of the property of acidity; and when united in a certain proportion, the properties of neither appear in the compound.

There are other substances besides the alkalis which act in opposition to acids, and which saturate equally the acid properties. Thus, the earths neutralize acids in combining with them, and form compounds similar in their general properties to those which the alkalis form with the acids. The greater number of the earths possess even the most characteristic alkaline properties, particularly that of changing the blue and purple colours of vegetables to a green. There exists, therefore, a strict analogy between these two orders of chemical agents.

But this analogy is still farther extended. When the metals are united with oxygen, they acquire the power of combining with acids, and of neutralizing completely the acid properties, forming compounds which in their general character bear a resemblance to the compounds which the acids form with the alkalis and earths.

Thus, in the most important chemical character of these substances, that displayed in their relation to acids, these three classes, Alkalis, Earths, and Metallic Oxides, are strictly connected; and the constitution of the last being known, analogy would have justified the conclusion, that the others are of a similar nature, or that the earths and alkalis consist probably of metallic bases combined with oxygen.

This analogy was accordingly extended to the earths. It was often supposed that they are metallic oxides, and attempts were made, though without success, to reduce them to the metallic form. But the same analogy does not appear to have been extended to the alkalis, or, if it was, it was only by a very remote and loose conjecture.

This appears to have arisen, partly from the peculiar properties of the alkalis being much less similar than those of the earths to the properties of the metallic oxides, but principally from another circumstance,—the composition of one of them, ammonia, having been established, and having apparently no relation to metallic matter or to oxygen. At an early period of pneumatic chemistry, it was found to consist of nitrogen and hydrogen. This led chemists aside from the analogy they might otherwise have pursued: the two fixed alkalis were supposed to be of similar constitution; and in the conjectures that were formed with regard to this, either nitrogen or hydrogen was supposed to be the alkaline principle, and to be united with some of the earths, as forming the fixed alkalis.

By the splendid discovery of the composition of the alkalis and earths, the original analogy has been fully established. Mr Davy, led by the law which he had discovered to regulate the decompositions produced by galvanism, submitted the two fixed alkalis to the action of this power; he effected their decomposition, and demonstrated that they consist of metallic bases combined with oxygen. He extended his investigations to the earths, and has been equally successful in proving that they also are metallic oxides, or that their bases are metallic, and are combined with oxygen. After these discoveries, ammonia, which is so strictly connected with the alkalis in properties, appeared insulated in composition. Mr Davy submitted it anew to analysis, and discovered, what before had not been suspected, that oxygen enters into its composition. It appeared, therefore, to be an oxide with a compound base. But the experiments of the Swedish Chemists, Berzelius and Pontin, already stated, and confirmed by those of Davy, have farther discovered that this base is of a metallic nature : and thus the analogy which connects all the substances distinguished by the important chemical property of neutralizing acids into one series, is extended to their composition ; and all the salifiable bases, as they have been named, comprehending the alkalis, earths, and metallic oxides, are demonstrated to be of similar chemical constitution. This must be regarded as a happy generalization, established by the genius and labours of one philosopher.

Though these substances are thus connected, I have already stated that there are grounds for still regarding them as subdivisions, at least, of a class, and for preserving the ancient distinctions between them. Though the bases of all of them may be metallic, yet those of the alkalis and earths have some peculiarities, both in their physical and chemical properties, when compared with what are usually ranked as metals. And considering them in their oxidated state, the alkalis, except in the leading property of neutralizing the acids, and forming saline compounds, are very different from the metallic oxides, and are much more active in their chemical agencies. The earths form the order which in some measure connects them, having strict relations in properties with each.

Some of the earths even approach so near in their general properties to the alkalis, that it has been proposed to transfer them from the one order to the other. Vauquelin made this change of arrangement with regard to two of them, barytes and strontites ; and he has been followed by Fourcroy. There are sufficient reasons, however, for rejecting this innovation. Classes of substances, founded on agreement of properties, cannot in general be kept so distinct, but that a gradation from one to another may be traced ; and wherever the limits are placed, there will be some room for objection. In the present case, if we place ammonia at the extreme of the one class, and silex at that of the other, though these substances are very dissimilar, there is a series which connects them ; and if we form the substances which compose this series into two groups, we can scarcely assign them characters appropriate, and at the same time exclusive, so that where-ever we draw the line of distinction, the substances on either side may not be connected. It is preferable, therefore, in such a case, to adhere to the division which has long been established : if we were so far to deviate from it as to transfer barytes and strontites from the earths to the alkalis, it would be found difficult to assign a reason for not doing the same with lime ; and if lime be received, magnesia and argil may also claim a place. The three alkalis, as they have been named, are distinguished by their much greater solubility in water, and their stronger affinity to it ; so that ammonia, though in the elastic form, combines with it instantly, and potassa and soda attract it from the atmosphere, while the most soluble of the earths requires at least twenty parts for its solution; by their solubility in alkohol, in which the others are insoluble; by their greater fusibility and volatility; and, generally speaking, by the greater activity they display in their chemical actions.

CHAP. I.

OF AMMONIA AND ITS BASE.

THE name of Volatile Alkali was given by the older chemists to a transparent liquid, which, in addition to the general alkaline qualities, is volatile, and has an extremely pungent smell. This however is not the alkali in its pure state, but a solution of it in water. From this Dr Priestley shewed that the alkali may be procured by the application of a modern heat. It is volatilized, and, when collected above mercury, exists as a permanent gas, at least at any moderate natural temperature. To this substance the name Ammonia is given; its solution may be named Liquid Ammonia, as by combination with water its properties are not materially altered.

Ammonia, I have stated, was considered as a compound of nitrogen and hydrogen. This was not inferred from its formation, for when these two gases are mixed together, the elasticity of each is an obstacle sufficient to counteract their mutual affinity; their particles do not combine, nor can their combination even be effected as that of some other mixed gases can, by transmitting the electric spark through the mixture, or exposing them in any other way to a high temperature.

The first observation that could have suggested any thing as to the composition of ammonia, was made by Dr Priestley,—that on taking the electric spark or explosion in a quantity of the gas confined over quicksilver, its volume is enlarged; the enlargement, by repeating the operation sufficiently, being so considerable, that the gas occupies three times the space it before did. Its properties are at the same time changed; it is no longer absorbed by water, and is highly inflammable. A similar change was produced in it by transmitting it through a red hot earthen tube, and by heating in it pieces of porcelain, and various other solid substances. And afterwards Dr Priestley found, that by heating certain metallic oxides, they were reduced to the metallic state, water appeared, and the residual air seemed to be nitrogen gas *.

The nature of these experiments, and the rationale of their result, is now sufficiently evident. By exposing the alkaline gas to heat excited either by the electric spark, the solar rays, or that of ignition, its component parts are separated; and as hydrogen in its state of gas is much rarer than the alkaline gas, the space occupied by the gases thus separated, is much greater than that which they occupied when they were combined. Hence also, after these experiments, the gas is not absorbed by water, as

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* Priestley's Experiments on Air, vol. ii. p. 389. Ibid. p. 396.

neither nitrogen nor hydrogen is; and it is highly inflammable. The reduction of the metallic oxides is owing to the affinity of hydrogen to oxygen, in consequence of which the oxygen united with the metal combines with the hydrogen of the ammonia, and forms a small portion of water; the metal appears in its metallic state; and the nitrogen, the other component principle of the alkali, being freed from its state of combination, assumes the gaseous form. Dr Priestley, however, did not draw from his experiments the just conclusion, or place the theory of them in a clear light.

Scheele likewise observed the decomposition of ammonia, and the production of nitrogen gas, particularly in the detonation of a preparation named Fulminating Gold, which is a compound of ammonia and oxide of gold *. Bergman observed the same facts, and gave a theory of the detonation of this preparation, on the supposition that the ammonia it contained is decomposed †. Both these chemists regarded it as a compound of phlogiston and nitrogen gas, without affixing perhaps a very precise idea to the former term.

Berthollet first communicated precise ideas on the nature of ammonia, and attempted to determine the proportions in which its constituent parts are combined. Reviewing the experiments of Priestley and Scheele, and finding, that in the former, a species of inflammable air was produced from the decomposition of ammonia; and in the latter, a species of what was then termed phlogis-

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* Treatise on Air and Fire, p. 141.

† Chemical and Physical Essays, p. 159.

ticated air, he undertook experiments by which its composition might be exactly ascertained. He first endeavoured to determine this, from the products which the salt formed by the union of ammonia with nitric acid affords, when decomposed by heat; and finding that a considerable quantity of water was obtained, which did not pre-exist in the salt, he was enabled, by the discovery of the composition of water, which had been previously made, to infer, that this water had been formed in the experiment, and that the hydrogen, which is one of its constituent parts, is derived from the ammonia. Again, having observed, that when a particular acid, the oxymuriatic, which parts readily with oxygen, is added to liquid ammonia, an effervescence takes place, he examined the gas disengaged, and found it to be nitrogen gas. He concluded, that in this experiment the oxygen of the acid combined with the hydrogen of the ammonia, and formed water; and the nitrogen gas disengaged he regarded as its other constituent principle. Hence, from the two experiments he inferred, that hydrogen and nitrogen are the component parts of this alkali; and on this theory of its composition, he found it easy to give a satisfactory explanation of the experiments of Priestley and Scheele, which were even proofs of its truth.

He sought to determine the proportions in which these principles are united to form ammonia. The experiment which he regarded as affording the most accurate result, was that of decomposing the ammoniacal gas by the electric spark;—it was thus resolved into the two gases;—a quantity of oxygen was then added in the eudiometer of Volta; and, by detonation with the hydrogen, water was formed, and the nitrogen remained. From this experiment he concluded, that in ammonia, 121 parts by weight of nitrogen are combined with 29 of hydrogen, or in 100, 80.7 with 19.3*. Mr Davy, from experiments made at a later period, in which ammonia was decomposed, by transmitting it through an ignited tube, and detonating the gas obtained with a portion of oxygen, inferred, that ammonia consists of nitrogen and hydrogen, in proportions almost precisely the same as those assigned by Berthollet †, being 80 of nitrogen, and 20 of hydrogen.

It was endeavoured to confirm the composition of ammonia by synthesis; but this was found more difficult to accomplish, the two gases not being combined when presented to each other, even when the electric spark is taken in the mixture. It had been observed, however, by different chemists, and particularly by Dr Priestley, that in different experiments, ammonia appeared to be formed; or it was produced, where it did not pre-exist in the materials. These were repeated and diversified by Dr Austin, who ascertained the principle on which the success of them depended.

In presenting two gases to each other, the obstacle to the effective exertion of their mutual affinity is the elasticity of each. If therefore they meet when disengaged from substances in which they exist, before they have fully assumed the elastic form, their union may take place. This Dr Priestley termed the action of gases on each other in their *nascent state:* and the success of this arrangement is well exemplified in the formation of ammonia.

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* Mémoires de l'Acad. des Sciences, 1785, p. 316.

† Chemical Researches, p. 61.

It had been known, that in the action of nitric acid on tin, ammonia is formed. The composition of ammonia being known, and the principle now stated being established, it was not difficult to explain this formation. Nitric acid is a compound of oxygen and nitrogen, and in its usual state contains also a portion of water. Tin is a metal which has a strong attraction to oxygen, and is capable of combining with a large quantity of it; it attracts therefore oxygen both from the acid and the water; and the nitrogen of the one, and hydrogen of the other, being disengaged, and coming in contact in their nascent state, unite and form ammonia.

Dr Austin repeated this and other experiments, and diversified them so as to establish the circumstances which are requisite for the formation of this compound. He found that it was not necessary that both the gases should be in the nascent state; but that if nascent hydrogen were presented to gaseous nitrogen, ammonia was formed. In a tube, containing nitrogen gas, inverted and placed in quicksilver, he put a small quantity of iron-filings, moistened with water; in twenty-four hours a sensible portion of ammonia was formed, the iron attracting the oxygen of the water, and the hydrogen in the moment of its disengagement combining with the nitrogen. The experiment even succeeds in atmospheric air, though a longer time is requisite; and hence a source of fallacy attending the use of the mixture of iron-filings and sulphur, moistened, as a eudiometer, part of the nitrogen being abstracted. To this Dr Austin ascribes, with probability, the great diminution, which Scheele observed, of atmospheric air from such a mixture—amounting to 27 or 28 in the 100.

Though the experiment succeeds when nascent hydrogen is presented to nitrogen, it does not succeed when the circumstances are reversed, or when nascent nitrogen is presented to gaseous hydrogen. This Dr Austin tried by mixing hydrogen gas with nitrous gas,—a compound of oxygen and nitrogen, and exposing the mixture to iron-filings; the metal attracts the oxygen of the nitrous gas, and disengages the nitrogen; but this, though in contact with hydrogen gas, does not combine with it; a difference of result which Dr Austin ascribes to the great rarity of the hydrogen gas, the particles of which are probably at such distances, when it exists in its elastic form, that the particles of nitrogen are unable to exert that affinity which becomes effective when the hydrogen is in a denser state *.

Ammonia, from these experiments, analytic and synthetic, appeared to be proved to be a compound of hydrogen and nitrogen; the proportions, as determined by Berthollet and Davy, being 80 of nitrogen and 20 of hydrogen.

The experiments from which this was inferred, could never, however, be considèred as so accurate, as to preclude entirely every source of fallacy. This I remarked in the former edition of this work with regard to its analysis; the experiment, whether in the mode performed by Berthollet, of decomposing it by detonation with oxygen, or in that executed by Davy, by transmitting it through an ignited tube, and then detonating it, being liable to fal-

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* Philosophical Transactions, vol. lxxviii. p. 379.

lacy, both from the presence of water in the gas, and from the possibility in the analysis of a portion of its nitrogen or hydrogen being combined with oxygen. And with regard to the synthetic experiments, little more could be inferred from them, than the formation of the ammonia, when hydrogen and nitrogen are presented to each other, in a state in which the operation of other principles is not excluded.

Mr Davy having discovered the existence of oxygen in potassa and soda, was led, from analogy, to suppose that oxygen must also be an element in the composition of ammonia; and on attending to the experiments by which its composition had been supposed to be established, he found, that they did not preclude this conclusion. He therefore submitted it anew to analysis, and soon satisfied himself that it does contain oxygen. When charcoal was ignited in very pure and dry ammoniacal gas by a galvanic battery, a great expansion of the aërial fluid took place, and carbonate of ammonia was formed. Its analysis was executed with still more accuracy. Pure ammonia, in the state of gas, was passed from one gazometer into another, over iron-wire ignited in a platina tube, two curved glass tubes being connected with the platina tube in such a manner that they were surrounded by a freezing mixture; the gas passed through one of these tubes before entering the platina tube, and after having passed through this, it was conducted through the other. In the cooled glass tube, transmitting the pure ammonia, no sensible quantity of water was observed to be deposited; but in the other, through which the gas passed after it had been exposed to a red heat, moisture was very evident, and the gas appeared in the gazometer densely clouded. This indicated, therefore, the formation of water from the decomposition of the ammonia, unless it could be supposed, what is not very probable, that the hydrogen and nitrogen gases, into which the ammonia is converted at the temperature of ignition, are capable of holding less water in solution or suspension than the ammoniacal gas contained. But farther, after the ammoniacal gas had been passed several times through the ignited tube from one gazometer to the other, the iron-wire in the tube was found to be converted superficially into oxide, and had gained in weight $\frac{44}{100}$ parts of a grain; about $\frac{4}{10}$ of a grain of water were collected from the cooled glass tubes by means of filtrating paper; and 33.8 cubic inches of gas were expanded into 55.3 cubic inches: and by detonation with oxygen, it was found that the hydrogen gas in these was to the nitrogen as 3.2 to 1 in volume. Mr Davy farther analysed ammonia, by taking the electric spark in it. In this experiment, it is known to be resolved into nitrogen and hydrogen gases; but the results he found to vary considerably, particularly from the presence or absence of humidity. In an experiment which was regarded as accurate, the weight of these two gases obtained was less by nearly $\frac{1}{11}$ than that of the ammonia employed; and this loss, Mr Davy inferred, could only be ascribed to the existence of oxygen in the alkali, part of which probably combined with the platina wires employed in the electrization, and part with hydrogen. The oxygen in ammonia, he infers, cannot well be estimated at less than 7 or 8 parts in the hundred, and it may exist even in a larger proportion, as the gases evolved may contain more water than the gas decomposed *.

In thus considering ammonia as a triple compound of nitrogen, hydrogen, and oxygen, it is easy to explain the phenomena, both of its formation and decomposition. In all the cases in which it is formed, oxygen is present, along with its other elements, in the substances from the decomposition or mutual action of which it is produced; and in its decomposition, the oxygen may either be abstracted by the decomposing substance, or may enter into combination with portions either of its hydrogen or nitrogen.

I have already stated, under the history of hydrogen, the experiments which appear to prove that the ultimate base of ammonia is of a metallic nature. They were first made by Berzelius and Pontin, by placing quicksilver, negatively electrified in the galvanic circuit, in contact with a solution of ammonia. Under this agency, the mercury increased in volume, and, when expanded to four or five times its former dimensions, became a soft solid. From this substance, quicksilver and ammonia are reproduced, by exposure to the atmosphere, oxygen being absorbed; and the same products are obtained by placing it in water, hydrogen beng evolved,—proofs that the ammonia is formed of the metallic matter which unites with the quicksilver, combined with oxygen. These experiments have been confirmed by Mr Davy, who diversified the process, and obtained the amalgam readily, by subjecting quicksilver, in contact with muriate or carbonate of ammonia, to

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* Philosophical Transactions, 1808.

the action of the negative galvanic wire. He obtained a similar result, by applying the de-oxidizing power of the base of potassa, or soda, either of these bases being united with quicksilver; and this compound being made to act on muriate of ammonia, the amalgam increased to six or seven times its volume, and the compound seemed to contain more of the ammoniacal base than that procured by electrical powers [*].

In these experiments, too, is presented a confirmation of the conclusion, that oxygen is an element in the composition of ammonia, Mr Davy having found, after the Swedish Chemists, that this amalgam thrown into water produces ammonia, and at the same time evolves hydrogen —a proof of the oxygen of the water being abstracted. He farther found, that when it is confined in a given portion of air, the volume of the air enlarges from the production of ammoniacal gas, equal to one and a half, or one and three-fifths of the volume of the amalgam, while a quantity of oxygen equal to one-seventh, or one-eighth, of the ammonia disappears: quicksilver too is reproduced. A similar proof is derived from the production of sulphate of ammonia and sulphur, when it is immersed in sulphuric acid.

This metallic matter could not be obtained by itself. I have already stated, that it is uncertain whether it is derived from the hydrogen or the nitrogen of the ammonia, or from both, or whether both these gases are peculiar forms of this metallic matter, which, to distinguish it, whatever may be its nature or origin, may be named Ammonium. Its existence as the base of ammonia, however, and its combination with oxygen, as forming that alkali, sufficiently confirms the analogy in constitution between this and the other alkalis; and when the relations which seem to subsist between hydrogen, nitrogen, and oxygen, are better understood, more precise ideas will be established of the nature of ammonia and its base.

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[*] Philosophical Transactions, 1808.

AMMONIA cannot be formed in any considerable quantity by the direct combination of its constituent principles. It is produced by indirect processes, and usually from the decomposition of animal substances by heat, the elements of these combining, partly, so as to afford this alkali.

If the bones of animals be exposed to heat in an iron still, this formation of ammonia takes place: There is formed, at the same time, from other combinations of the principles of the animal matter, a quantity of carbonic acid, with which the ammonia is combined; and this compound is obtained partly solid, and partly dissolved in a portion of water which distils over, forming what were named the salt and spirit of Hartshorn *. Other animal substances furnish it, as do also some varieties of vegetable matter. The soot of coal, which is of vegetable origin, affords it combined with some of the acids, and is used to procure it on a large scale.

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* Dr Woodhouse has affirmed, that the product of ammonia is five times greater, when this process is performed in an apparatus into which the air is admitted, than when it is excluded by close luting, owing, as he supposes, to the nitrogen of the atmosphere combining with hydrogen from the bones. Philos. Mag. vol. vii. p. 86.

The ammonia obtained by such processes is impure, being mixed in particular with a quantity of empyreumatic oil, which gives it a very fœtid odour, and from which it is difficult to free it. The most effectual method is, to combine the ammonia with an acid, evaporate the liquor, and obtain the ammoniacal salt in a solid state. A process of this kind, which is afterwards to be described, is carried on, on a large scale, to obtain a salt which is used in large quantities in some of the arts,—the muriate of ammonia, or sal ammoniac of commerce; and the chemist, instead of following the different steps now stated, always avails himself of this salt to obtain pure ammonia.

One part of this muriate of ammonia is reduced to powder, and mixed in a retort with two parts of newly slaked lime: If heat be applied to the retort, ammonia is copiously disengaged in the elastic state, the lime dislodging it by combining with the muriatic acid, which is the other ingredient of the muriate of ammonia. As this gas is largely absorbed by water, if it is to be examined in the gaseous form, it must be received in jars filled with quicksilver, the extremity of the tube of the retort being introduced beneath them, filled and inverted in the quicksilver bath.

As it is inconvenient preserving and using it in this form, it is, for common purposes, always used in combination with water, forming what is named Liquid Ammonia: This is prepared merely by connecting a retort with the mixture of muriate of ammonia and lime in the above proportions, and about thrice their weight of water, with the bottles of Woolfe's apparatus containing water. The retort being placed in a sand bath, and a moderate heat applied, the ammonia is expelled, part of it is condensed in the first bottle by the water which distils over from the retort, the rest is absorbed by the water in the other bottles. In the large way, the distillation is performed in an iron still, a larger proportion of water being added, and this being condensed by being passed through a tube placed in a refrigeratory, and terminating in a range of receivers.

Ammonia, at any temperature above —56° of Fahrenheit, exists when uncombined in the gaseous form. At that temperature, according to the experiments of Guyton *, it becomes liquid, (returning to the elastic state as the temperature rises),—a condensation which it is not improbable is assisted by the water, which, from its strong attraction to that fluid, it will hold combined with it, even in the gaseous form. Its specific gravity at the temperature of 60° of Fahrenheit is 0.000715. It is to that of atmospheric air as 600 to 1000. 100 cubic inches, according to Mr Davy, weigh 18 grains. In its gaseous form it is colourless, but not inodorous; on the contrary, its smell is strong and pungent; it inflames the skin; animals are killed by immersion in it, and the lungs are found, on dissection, to be inflamed.

This gas extinguishes combustion. It is itself slightly inflammable. When a kindled match is immersed in it, the flame, before it is extinguished, is enlarged, and is of a pale yellow colour at the edges; if mixed previously with two-thirds of atmospheric air, it kindles and gives a white lambent flame.

Ammonia has a strong attraction to water, and is absorbed by it with great rapidity; caloric, as might be expected, being extricated during the absorption. Ice is li-

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* Annales de Chimie, t. xxix. p. 279.

quefied by exposure to it, and cold produced,—a proof of rather a singular fact, that less caloric is evolved from the condensation of a gas than is absorbed by the liquefaction of a solid. Below 50° water takes up rather more than one-third of its weight of the gas, a saturated solution of it containing, according to Mr Davy, in 100 parts, 25,37 of ammonia. The specific gravity of the water is diminished by the absorption, being, when saturated, not more than 9054. The solution, according to Vauquelin, crystallizes at —40° ; and concretes into a jelly, losing also its odour, at —58°. By a heat not exceeding 150° it is decomposed, and the ammoniacal gas expelled.

The solution of ammonia in water is the form under which it is used in chemistry and medicine. Mr Davy has given a table from which its strength may be estimated from its specific gravity *.

100 parts Specific grav.		Ammonia.	Water.
.9054	contain	25,37	74,63
.9166		22,07	77,93
.9255		19,54	80,46
.9326		17,52	82,48
.9385		15,88	84,12
.9435		14,53	85,47
.9476		13,46	86,54
.9513		12,40	87,60
.9545		11,56	88,44
.9573		10,82	89,18
.9597		10,17	89,83
.9619		9,60	90,40
.9684		9,50	90,50
.9639		9,09	90,91
.9713		7,17	92,83

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* Chemical Researches, p. 68.

Ammonia exerts no important agency on oxygen, hydrogen, or nitrogen gases. No additional quantity of either of its ingredients can be combined with it. Mixed with oxygen gas, no action takes place at a low temperature; but if a burning body be introduced, or if the mixture be passed through a red hot earthen tube, the ammonia is decomposed, its hydrogen and the oxygen combining together. It unites with some of the primary inflammables, as I shall afterwards have to state. It acts, too, on some of the metals, promotes their oxidation, and combines with several of their oxides. It unites with all the acids, forming neutral salts. Its affinities to the acids appear inferior to those of the other two alkalis; but this, according to Berthollet's views, is owing to its volatility; and as a given weight of it saturates more of the acids, he regards it as exerting a more energetic action.

CHAP. II.

OF POTASSA AND ITS BASE.

THIS alkali has been long known to chemists, and by various appellations. Being in general obtained from the burning of vegetables, it was named Fixed Vegetable Alkali: as it is the basis and distinctive ingredient of the saline matter known in commerce by the name of potashes, it was termed Potasse by the authors of the new nomenclature, a name which by some chemists has been received into the English language, while by others that of Potash has been preferred. Dr Black gave it, from Pliny, the name of Lixiva. Mr Kirwan imposed that of Tartarin; and by the London College it was named Kali. I have used Potassa, a name, I believe, preferable to the others, as distinct from the potash of commerce, and as analogous in termination to the names of the other alkalis, and conformable to the English idiom.

From the analogy of potassa with ammonia, it had often been conjectured to be a compound body, and some facts had been stated, in proof of its production, where it did not previously exist, as in the process in which nitre is formed. Chaptal, from some observations of this kind, had supposed that it is a compound of nitrogen and lime. At a later period, experiments were made by Guyton and Desormes, in which potassa appeared to be produced; from which they inferred, that it is a compound of lime with hydrogen. These, however, were never very decisive, and being examined by Darracq, were found altogether insufficient to establish the conclusion that had been drawn from them *.

Nothing, therefore, was truly known with regard to the nature of this alkali; and the discovery of its composition by Mr Davy, when it was accomplished, shewed how imperfect the analogies were from which these conjectures had been drawn. The discovery will ever be regarded as one of the most important in chemistry, as having introduced to the knowledge of the chemist a class of substan-

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* Mémoires de l'Institut. National, tom. iii. p. 322; Philosophical Magazine, vol. xi. p. 344.

ces altogether peculiar, and having little analogy with any before known, and as having established views which have the most extensive influence in the relations of the science.

Mr Davy, I have already remarked, was led to institute experiments with a view to decompose the fixed alkalis, by his previous discovery, that by the powers of galvanism the principles of bodies are separated, according to a certain law, some being attracted to the one galvanic pole, others to the other, and that the strength of these attracting forces are proportional to the energy of the opposite electricities in the galvanic circuit, and to the conducting power and degree of concentration of the substances submitted to their action.

In his first attempts, he exposed the alkali dissolved in water to the action of the galvanic battery, but the water alone of the solution was decomposed. Potassa in fusion was then placed in the galvanic circuit; a vivid light, and appearances of the production of combustible matter were observed; on submitting the solid alkali, rendered a conductor of electricity by being very slightly moistened, to the galvanic action, these appearances were still better marked; and it was by this method that Mr Davy succeeded in effecting the complete decomposition.

" A small piece of pure potash, which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface, was placed upon an insulated disc of platina, connected with the negative side of the battery, in a state of intense activity, and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. Under these circumstances, a vivid action was soon observed to take place. The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the lower, or negative surface, there was no liberation of elastic fluid; but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces. These globules, numerous experiments soon shewed to be the substance I was in search of, and a peculiar inflammable principle, the basis of potash *." The platina, Mr Davy found, had no share in its production, as it was equally produced when other metals or even charcoal were employed for completing the electrical circuit. The phenomenon, too, was quite independent of the presence of air.

As in the decomposition of compound substances by galvanism, Mr Davy had found, that when combustible bases are developed at the negative side, oxygen is evolved at the positive side; it was reasonable to conclude, that this happened in the above experiment, and that the effervescence observed at the part of the potassa in immediate contact with the positive wire, was due to the disengagement of oxygen gas. He accordingly found, performing the experiment in glass tubes, so as to collect the aërial product given out at the positive surface, that this, on the most delicate examination, proved to be pure oxygen; and unless an excess of water was present, no gas

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* Philosophical Transactions, 1808.

was evolved from the negative surface, nothing being produced there but the inflammable globules.

By these analytic experiments, therefore, potassa is proved to be a compound of a peculiar substance, highly inflammable, and having metallic lustre, with oxygen. And this Mr Davy soon confirmed by synthetic experiments.

He found, that the metallic lustre of this inflammable substance immediately became destroyed in the atmosphere, and a white crust formed upon it, which was pure potassa. This was soon dissolved by attracting humidity from the air; a new quantity was formed on the surface, until the whole disappeared, and had formed a saturated alkaline solution. When the globules were placed in tubes containing atmospheric air, or oxygen gas, an absorption of oxygen took place, and a crust of alkali was formed. When they were strongly heated, confined in given portions of oxygen, a rapid combustion with a brilliant white flame was produced, and they were converted into a white and solid mass, which was found to be potassa: oxygen was absorbed, and nothing emitted which affected the purity of the residual air.

Thus, it appears, both by analysis and synthesis, that potassa is a compound of a peculiar inflammable base with oxygen, this conclusion resting apparently on the same kind of evidence as that from which the constitution of other chemical compounds is inferred. From subsequent experiments, Mr Davy endeavoured to determine the proportions of these elements. From the products of the combustion of the base, compared with the quantity of oxygen absorbed, he inferred, taking the mean of two experiments, that potassa consists of 86.1 of base, and 13.9 of oxygen. From the results of the decomposition of water by the base, the proportions indicated were 84 of base, and 16 of oxygen. The mean of these will be 85, and 15.

These experiments have been confirmed, so far as relates to the decomposition of the alkali by other chemists; and indeed the experiment can be performed without difficulty, with a galvanic battery of not very high powers. One of 100 plates of 6 inches square is sufficient.

But a more important confirmation of the discovery is that which has been received from an experiment performed by Gay Lussac and Thenard. It occurred to these chemists, that potassa might be decomposed by causing a substance to act on it having a strong attraction to oxygen. They put clean iron-filings into a gun barrel, bent, so that the filings in the curvature could be raised to a sufficient heat, by the barrel being placed across a furnace. With one extremity of it, a tube with a stopper is connected containing solid potassa. When the iron-filings in the barrel are brought to a white heat, the alkali in the tube, which has been previously kept cold by a freezing mixture, is melted, by applying heat to it by a portable furnace, and it is allowed to run through a small aperture upon the iron-filings. It suffers decomposition, the iron attracts its oxygen, and the inflammable base is sublimed to the other extremity of the tube, which is kept cold, so as to condense it; a tube of safety, containing a little mercury, being connected with the extremity, to allow of the disengagement of any aërial matter, and at the same time exclude the air. Hydrogen gas is disengaged during the process, which appears to be derived from the decomposition of water contained in the alkali, and the result is most successful when the alkali is in its driest state. The base of the alkali is obtained in the form of brilliant laminæ, adhering to the sides of the gun-barrel; there is also found in the curvature, where the filings were contained, an alloy of it with iron. According to Mr Davy, who has performed the experiment with success, the base thus obtained is rather heavier than that procured by electricity, probably from containing a little iron [*].

This interesting experiment of course precludes the conjecture of this peculiar substance owing its origin in any manner to the action of galvanism,—a suspicion which might have been perhaps entertained, had it not been obtained by a process of this kind; and it enables the chemist to obtain this substance in larger quantity than it can well be procured by galvanic action.

To the matter discovered by these researches, as the base of potassa, Mr Davy has given the name of Potassium, the termination of this name being that assigned to metals, and this substance being presumed to be metallic. It will be proper to state its properties before proceeding to the history of the alkali.

Potassium, at the temperature of 60° of Fahrenheit, appears in the form of small globules, possessing the metallic lustre and opacity, and having the general appearance of quicksilver, so that by the eye it is not easy to distinguish between them. At this temperature, however, it is rather imperfectly fluid, so that it does not easily recover its globular form; at 70° it is more liquid and mobile; and at 100° is so completely so, that different globules can be easily run into one. At 50° it becomes a soft and malleable solid, which has the lustre of polished silver; and at 32° it becomes harder and brittle, displaying when broken a crystallized texture. Though so fusible, it is not very volatile, but requires a temperature approaching to a red heat to convert it into vapour. It condenses unchanged. It is a perfect conductor of electricity, and is also an excellent conductor of heat.

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[*] Philosophical Magazine, vol. xxxii. p. 89. 276.

In these properties it obviously has the closest resemblance to metals; and it might therefore be expected also to resemble them in their most characteristic property, that of density. It is very singular, however, that so far from this it is lighter than water, or even alkohol, or ether. Mr Davy found that it did not even sink in naphtha twice distilled, the specific gravity of which was about .770. Its specific gravity he estimates, compared with that of water, as 6 to 10 at 62° of Fahrenheit. It is therefore the lightest fluid known. In its solid form it is rather heavier, but still when cooled to 40° it swims in distilled naphtha.

Its chemical relations are not less singular than its physical properties.

It combines with oxygen slowly, and without flame, at all temperatures below that of its volatilization, but at this temperature combustion of it takes place; the heat is intense, and the light white and vivid. It appears to combine with different proportions of oxygen, at least an oxide of it in a lower state of oxidation than potassa can be obtained. Thus, when heated slowly in a quantity of oxygen not sufficient to saturate it, and at a temperature not higher than 400°, its colour changes to a reddish brown; the oxygen is absorbed, and when cold, a substance is obtained of a greyish colour, consisting partly of potassa, and partly of the potassium in a lower degree of oxidation. This by being heated in air, or exposed to water, is converted into the alkali. The same substance can be formed by fusing potassium with dry potassa. Potassium inflames in other gases which can afford oxygen, as in oxymuriatic acid gas. It is so liable to oxygenation, that it is difficult to preserve it unchanged. The best method is to keep it in naphtha; for although it does not sink in that fluid, it is enveloped by a film of it, which protects it from the action of the air.

When heated in hydrogen gas, at a degree below its point of vaporization, it diminishes in volume, and the gas explodes with the production of alkaline fumes, when it is allowed to pass into the air; a portion of the potassium appears, therefore, to have been dissolved; but by cooling this is in a great measure deposited, as the gas loses its property of detonating spontaneously.

Potassium, when brought into contact with water, decomposes it with great violence; an explosion is produced with flame, and potassa is formed. Placed on ice it instantly burns with a bright flame, melting the ice. So strong is the action of this substance on water, that it discovers, by the decomposition it produces, the smallest quantity of water in other liquids, as in alkohol, or ether.

Potassium thrown into solutions of the mineral acids inflames and burns on the surface, and the compound of potassa with the acid employed is formed.

Potassium combines with the primary inflammables. When brought in contact with phosphorus under exposure to air, both bodies become fluid, burn, and phosphate of potassa is formed. When the experiment is made under naphtha, so as to exclude the air, they unite and form a compound less fusible than either of its ingredients. In its appearance it is perfectly similar to the compounds of metals with phosphorus, the metallic phosphurets as they are named; it is of the colour of lead, and has a lustre similar to that of polished lead. Exposed to the air it combines slowly with oxygen, and is converted into phosphate of potassa.

When potassium is brought in contact with sulphur in fusion, under the vapour of naphtha, so as to exclude the air, they combine rapidly with the evolution of heat and light, and a grey substance, in appearance like artificial sulphuret of iron, is formed, a little sulphuretted hydrogen being evolved. When the union is effected in the atmosphere, inflammation takes place.

With the metals potassium enters readily into combination. With mercury it produces some singular results. When one part of it is added to eight or ten parts of mercury in volume at 60° Fahrenheit, they instantly unite and form a substance exactly like mercury in colour, but which has less coherence, for small portions of it appear as flattened spheres. When a globule is made to touch a globule of mercury about twice as large, they combine with considerable heat; the compound is fluid at the temperature of its formation; but when cold it appears as a solid metal, similar in colour to silver. If the quantity of the basis of potassa is still further increased, so as to be about $\frac{1}{70}$ the weight of the mercury, the amalgam increases in hardness, and becomes brittle. The solid amalgam, in which the basis is in the smallest proportion, seems to consist of about one part in weight of base and 70 parts of mercury, and is very soft and malleable.

When these compounds are exposed to air, they rapidly absorb oxygen ; potassa which deliquesces is formed ; and in a few minutes the mercury is found pure and unaltered. When a globule of the amalgam is thrown into water, it rapidly decomposes it with a hissing noise ; potassa is formed, pure hydrogen disengaged, and the mercury remains free.

The fluid amalgam of mercury and this substance dissolves all the metals ; and in this state of union, mercury acts on iron and platina.

When potassium is heated with gold, or silver, or copper, in a close vessel of pure glass, it rapidly acts upon them ; and when the compounds are thrown into water, the fluid is decomposed, potassa formed, and the metals appear to be separated unaltered.

It reduces the metallic oxides, when heated with them ; and when the potassium is in excess, it combines with the reduced metal. In consequence of this property it decomposes flint glass and green glass, reducing the metallic oxides they contain, and forming potassa which dissolves the glass. At a red heat it acts even on the purest glass, attracting part of the oxygen of the alkali in the glass, and forming the substance which is potassium in the first degree of oxygenation.

The question naturally occurs, is this substance metallic ? It has not indeed one of the most characteristic of the metallic properties, that of density ; but it has all the others, opacity, lustre, and malleability. And it displays in its chemical actions metallic properties, combining with the metals without changing their general properties, and forming compounds with the primary inflammables, similar in their appearance to those which the common metals form. The conclusion of Mr Davy, therefore, that potassium is a metal, is that perhaps which must be received.

Potassa. Having stated the properties of the Base of Potassa, as they have been ascertained by Mr Davy, by whom only this substance has been examined, I have to proceed to the history of the alkali itself. The great source from which it is procured, is the combustion of vegetable matter. It has been discovered, indeed, in the mineral kingdom, but only as an ingredient of some fossils, and in small quantity; and for the numerous purposes to which it is applied in the arts, it is always obtained by burning vegetables. It is generally prepared in countries in which wood abounds, and is imported to us from Russia and North America. The vegetable matter being burnt with an open fire, the ashes are collected, and lixiviated with water, which dissolves the saline matter; the solution is poured off from the undissolved matter, and is evaporated in large iron pots to a solid mass. This is the potash of commerce; it is of a grey colour, and generally becomes humid. When heated in a reverberatory furnace, the extractive matter it contains, and which appears to have been rendered soluble in water by the potash, is burnt out, and a portion of the water is dissipated. It then forms the pearl-ash of commerce, which is of a white colour, frequently with a tinge of green or blue, arising, as Scheele has shewn, from oxide of manganese, derived from the vegetable matter.

This product of saline matter is afforded in different quantities by different vegetables submitted to the same process. In general, the harder woods afford more than the spongy, shrubs more than trees, and herbaceous plants the largest quantity. Even different parts of the same vegetable afford different proportions, the branches affording more than the trunk, and the leaves more than the branches. From different plants it is obtained in different states of purity with regard to the alkali; that from the stalks of the vine is remarkably pure. The general conclusions, from an extensive series of experiments on this subject, made by order of the French government, under the inspection of the overseers of the fabrication of nitre, have been given by Pertuis, in a memoir, in which, as well as in one following it by Vauquelin, will be found much practical information *: 1st, Shrubs give three times, and herbaceous plants five times more ashes than large trees: 2d, The trunk of trees gives less ashes than the branches, and these less than the leaves: 3d, Plants in their state of maturity give more than they do either before or after that period: 4th, Plants burnt green give more, than when they are weighed green but dried before they are burnt. Tables are given by Pertuis, of the products from a great variety of vegetables. Two tables were also given by Mr Kirwan, from the same authority †. They are of less value than they might have been, as the quantity of saline matter

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* Annales de Chimie, tom. xix. p. 157. 194.

† Transactions of the Irish Academy, 1789, p. 35-6.

merely is stated, without any report as to its quality, or the quantity of potassa it contains.

It is a question of some interest, whether the alkali obtained by the process now described, pre-existed in the vegetable matter; or whether it has been actually formed during the combustion. It cannot be doubted but that part of it is derived from the former source, for plants contain salts having potassa for their base, and these being more or less decomposed during the burning, must furnish at least part of the saline matter obtained by the combustion. It is not, however, perfectly ascertained that the whole of what is obtained has had this origin. Nor do we know, whether the base of potassa exists as an element of vegetable matter, and is oxidated so as to form the alkali during the combustion.

The potash, or pearl-ash of commerce, is a very heterogeneous substance, or rather it consists of various substances, some of them combined, and some mixed together. The potassa it contains is always combined with carbonic acid, and with this are variable proportions of sulphate of potassa, muriate of potassa, siliceous earth, oxide of iron, and oxide of manganese. Different specimens differ in the quantities they contain of these ingredients. One pound of the best pearl-ash was found, by Mr Kirwan, to contain potassa 3477 grains; carbonic acid, 1290; water, 414; sulphate of potassa, 505; muriate of potassa, 36; earth, 38*.

The chemists have been accustomed to employ some other processes to obtain potassa, by decomposing various salts of which it is the base, and by which it is procured in a state less impure from the admixture of foreign substances, than in the potash of commerce. One of these processes, which was often employed, was to expose the saline matter, named White Tartar, to a red heat. It is a compound of potassa with a vegetable acid,—the Tartaric acid. This acid is decomposed by the high temperature, and a quantity of carbonic acid is formed from its decomposition, with which the potassa remains combined. This is freed from any insoluble matter by lixiviation with water, the ley is evaporated in a clean iron bason, and a white granular powder is obtained, formerly known by the name of Salt of Tartar, which is potassa imperfectly saturated with carbonic acid. A similar salt is procured from the deflagration of nitre with charcoal, or by exposing to a red heat a mixture of equal quantities of nitre and white tartar. All these, though purer than the potash or pearl-ash of commerce, are still contaminated with some foreign substances, especially with some earths and a little sulphate of potassa.

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* Transactions of the Irish Academy, 1789, p. 10.

Different processes have been followed to remove these, and obtain the alkali pure. The following is the one which was generally employed by chemists, and which is still a preliminary one to others, requisite to obtain it in a state of perfect purity. To the common pearl-ash of commerce, or to any of the analogous substances obtained by the processes just now described, a double quantity of quick-lime in powder is added; on this is poured as much water as is requisite to slake the lime; an additional portion of water is then added, so as to give the materials a thin consistence, and the mixture, without being exposed to heat, is to be allowed to stand two or three days, agitating it occasionally. The whole is then poured into a large glass funnel, the tube of which is obstructed with a piece of linen; the fluid part soon begins to filtrate through the mass, colourless and transparent; fresh portions of water are poured on the matter in the funnel, and this is continued until 8 or 10 times the weight of the potash originally employed have passed through the filtre. The liquor is removed, and either kept in glass vessels well stopt, or evaporated to a dry mass.

In this process, the lime attracts the carbonic acid from the potassa; and this alkali being extremely soluble, is dissolved by the water. The solution, however, is far from containing the alkali in a pure state. It is obvious that there are no adequate means employed to separate the other saline bodies, the sulphate and muriate of potassa; even a portion of the siliceous earth is held in combination by the alkali; and the whole of the carbonic acid is not abstracted, for when the greater portion has been removed by the affinity exerted towards it by the lime, the quantity of the potassa at length adds so much to the force of its affinity, that a proportion of carbonic acid is still retained in combination. The greater part of this carbonic acid, as well as any sulphuric acid, may be abstracted by a solution of the earth named Barytes, which attracts these acids with more force than lime; and this, as Mr Henry has remarked, is an easy mode of obtaining potassa, at least so far pure *.

The process generally followed, however, is one point-

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* Nicholson's Journal, 4to, vol. iv. p. 172.

ed out by Berthollet, by which the foreign substances contained in the solution of potassa prepared in the common mode may be abstracted, and the alkali obtained in a pure state. It is founded on the solubility of pure potassa in alkohol, while the other salts, as well as any earthy or metallic matter mixed with it, are insoluble. The first stage of this process is that which has just been described. When this has been performed, the liquor obtained by the filtration is to be evaporated until it become of a thickish consistence, and there is to be added to it about an equal weight of alkohol, allowing it to stand for some time in a close vessel. A quantity of solid matter, in part crystallized, is collected at the bottom; this is carbonate of potassa, with other saline substances, and a little silex, lime, and oxide of iron: above this is a small quantity of a very dark coloured fluid; this is the water of the alkohol with part of the alkali combined with carbonic acid. Floating above this, is another fluid of a lighter colour; it is to be poured off, being a solution of potassa nearly pure in alkohol, and is to be evaporated quickly in a silver bason placed in sand; a vessel of glass, or of almost any metal but silver, being acted on by the alkaline solution, which, if evaporated in such vessels, therefore, would be rendered impure. The evaporation is not carried far; and the liquor, on being allowed to remain at rest, again separates into two fluids: the heavier one, which is in small quantity, is a solution of the alkali still combined with carbonic acid: the lighter one above it is the solution of the pure alkali in alkohol; it is to be poured off, and again evaporated with a quick heat. On allowing it to remain for a day or two in a close vessel, it deposites transparent crystals of potassa, or, if evaporated until a pellicle appear on its surface, on cooling, the potassa passes into a concrete state without a regular crystallization; in either case, a quantity of deep-coloured liquor is separated, which is to be poured off; and the potassa preserved, carefully secluded from the air. It is thus obtained pure [*].

Another process, more economical, but less perfect, has been pointed out by Lowitz, which may answer, where it is not requisite that potassa should be in a state of complete purity. The solution of potassa, prepared as before from the mixture of the potash of commerce with lime, is evaporated until a thick pellicle appear on its surface: It is allowed to cool, and a quantity of saline matter, which is deposited, and which is principally the foreign salts that were mixed with the potassa, is to be removed. The liquor is again to be evaporated, and the pellicle which forms on its surface is to be skimmed off as it accumulates. When the pellicle ceases to be produced, and the matter does not boil up, it is to be removed from the fire, and allowed to cool with constant agitation. It is then to be dissolved in twice its weight of cold water, and the solution filtered, and evaporated (according to Lowitz's direction in a glass retort, but a silver bason must be preferable) until it begin to deposite crystals. If it should consolidate without crystallizing, a small quantity of water is to be added, and the mass heated again to render it fluid. By successive crystallizations, the liquor is left of a brown colour, which is owing to carbonaceous matter suspended in it; and when this has been deposited by rest, the clear liquor may again be evaporated and crystallized as long as the crystals are obtained colourless *. By this process, the different salts are, perhaps, nearly entirely separated from the potassa; but the silex, which is always originally combined with it, and the portion of lime with which it combines in the first stage of its purification, will probably still remain in combination; yet the quantities of these appear to be extremely inconsiderable; for Dr Kennedy, who has given a process for the preparation of pure potassa nearly the same with that of Lowitz, observes, that in saturating the potassa thus procured with an acid, and evaporating to dryness, the solid matter redissolves in water without leaving any earth, which it would do if any were present. He adds, that, by the most delicate tests of sulphuric and muriatic acids, (the nitrate of barytes and the nitrate of silver,) no portions of these acids are discoverable †.

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[*] Mémoires de l'Acad. des Sciences, 1783, p. 408.

Potassa obtained pure is a solid substance of a white colour, crystallizable from its saturated solution either in water or alkohol. The figures of the crystals are various, according to the extent of evaporation; they are sometimes in thin plates, or in slender needles, but when more slowly formed, in tetraedral pyramids in groups, or in octaedrons. These contain various proportions of water of crystallization; those which are slowly formed, and of a regular figure, contain about 0.43. They produce cold in dissolving in water, while the solution of dry uncrystallized potash is attended with an elevation of temperature.

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* Nicholson's Journal, 4to, vol. i. p. 164.

† Edinburgh Philosophical Transactions, 1799.

In either state when mixed with ice there is a rapid liquefaction, and the production of intense cold. Potassa has so strong an attraction to water, that it imbibes it rapidly from the atmosphere; less than its own weight is requisite for solution; one part of water at 60° dissolves two parts, the liquid being dense and of an oily consistence.

Potassa is easily melted; its melting point is about 360°; and by a heat, as Mr Chenevix has remarked, not exceeding a red heat, it is volatilized. When in fusion, it acts with energy on the greater number of the earths, and promotes their fusion, whence it is much used in mineral analysis.

It is extremely caustic: It quickly erodes the skin, and, mixed with animal matter, Berthollet found that it completely dissolved it; it occasions, at the same time, its decomposition, ammonia being formed, and a small quantity of charcoal separated. From its action on the skin it has a soapy feel.

A very minute quantity of potassa changes the vegetable colours to a green.

One of the distinguishing characters belonging to it, in common with the other alkalis, is its power of combining with the acids, and neutralizing them. It is inferior in this power to ammonia and soda, a larger quantity of it being requisite to saturate a given quantity of acid: This indicates a less energetic action; yet it decomposes the ammoniacal salts, which Berthollet of course ascribes to its greater fixity: It also decomposes several of the salts of soda, which is ascribed to the greater tendency to cohesion of the salts of potassa.

Another alkaline characteristic property is that of combining with oils and fats, and forming a saponaceous compound. The soap which potassa forms, does not easily become concrete.

By fusion with silex in a certain proportion, it forms glass, and with a less proportion of that earth, a compound soluble in water. Its solution dissolves argil.

Potassa does not act with much energy on the metals. It promotes the oxidation of some of them, however, when its solution is in a concentrated state. It combines with a number of their oxides, both in the humid way, and by heat. It unites too with sulphur and phosphorus, but not with carbon, hydrogen, nitrogen or oxygen.

Potassa, from the numerous combinations of which it is susceptible, is an important chemical agent, and is hence applied to many purposes in the arts, as in bleaching, in the manufacture of soap, of glass, &c. applications afterwards to be noticed. It is used in a number of the processes of pharmacy, and is employed in medicine as an antacid and lithontriptic.

Besides existing in vegetables, it is a principle, at least in combination with some of the acids, in several of the animal fluids. I have already remarked, too, that it has been discovered in the mineral kingdom as a constituent part of several fossils. It has been found particularly in volcanic products. Klaproth discovered it in the leucite. Vauquelin found it in that fossil as well as in the lava in which it is imbedded; and Dr Kennedy detected it in pumice. It has been discovered also in stones which cannot be suspected of volcanic origin, as in the zeolite of Ferroe, in the green feldspar of Siberia by Vauquelin, and in the lepidolite by Klaproth. Some of these contain 16 or 18 of potassa in 100 parts.

CHAP. III.

OF SODA.

SODA, the third of the alkalis, has been named Mineral or Fossil Alkali, as it is more abundant than either of the others in the mineral kingdom, and was at one time supposed exclusively to exist in it. It has received from the London College the name of Natron, there being reason to believe that it is the natron or nitrum of the ancients. Soda is the name by which it is generally known, and is unexceptionable. Du Hamel first shewed that it is a particular alkali, different from potassa *; and Margraaf added to the facts from which this conclusion was deduced, and pointed out some of its characteristic properties.

The nature of this alkali, previous to Mr Davy's discoveries, was equally unknown with that of potassa. The same analogy had led to the conclusion, that it is a compound; and similar conjectures had been formed as to its composition: magnesia was supposed to be its base, and to be combined in it, either with nitrogen or hydrogen, —suppositions which always rested on very imperfect grounds. Mr Davy having discovered the composition of potassa, of course submitted soda likewise to the same modes of analysis, and discovered that it, too, contains a substance of very peculiar properties, analogous to the base

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* Mémoires de l'Acad. des Sciences, 1736.

of potassa, though still essentially different from it, and that this base combined with oxygen forms soda.

When soda was submitted to the galvanic action, in the mode already described with regard to potassa, the results were similar; globules of a metallic appearance were produced at the negative surface, which often burnt at the moment of their formation, and sometimes exploded with violence, separating into smaller globules, which darted through the air in a state of vivid combustion. When these were produced, an aëriform fluid was disengaged at the positive surface, which proved to be pure oxygen. To effect this decomposition, a greater intensity of galvanic action was required than was necessary to decompose potassa.

The reproduction of soda from this substance was similar to that of potassa from the base of that alkali. When the base of soda was exposed to the air, a crust of alkali formed on its surface, and oxygen was absorbed. When heated confined in a portion of oxygen gas, a rapid combustion with a brilliant white flame took place, and soda was produced in the state of a solid white mass.

The theory of the operation in which soda is decomposed, is the same as that of the decomposition of potassa. The combustible base, like other combustible substances, is repelled by positively electrified surfaces, and attracted by negatively electrified surfaces; and the oxygen follows the contrary order. Hence their separation and evolution.

Mr Davy endeavoured to determine the proportions in which the base and oxygen are combined in soda, by experiments similar to those by which he determined the proportions of the elements of potassa. From the results of the combustion of the base of soda in oxygen gas, he inferred that 100 parts of soda consist of 80 of base, and 20 of oxygen. From the results of its oxidation by the decomposition of water, the proportions were estimated to be 77 of base, and 23 of oxygen. The mean proportions of these two modes are 78.5, and 21.5. The base of soda, therefore, combines with rather a larger proportion of oxygen than the base of potassa.

To the base of soda, Mr Davy, from its analogy to metals, has given the name of Sodium. From his statement I have given the following account of its properties.

Sodium is white, opaque, and when examined under a film of naphtha has the lustre and general appearance of silver. It is exceedingly malleable, and is much softer than any of the common metallic substances. When pressed upon by a platina blade, with a small force, it spreads into thin leaves, and a globule of the $\frac{1}{10}$th or $\frac{1}{12}$th of an inch in diameter is easily spread over a surface of a quarter of an inch, and this property does not diminish when it is cooled to 32° Fahrenheit.

It conducts electricity and heat in a similar manner to the basis of potassa; and small globules of it inflame by the galvanic spark, and burn with bright explosions.

Its specific gravity is less than that of water. It swims in oil of sassafras of 1.096, water being one, and sinks in naphtha of specific gravity .861. By mixing together oil of sassafras and naphtha, until a fluid was formed in which the globule of sodium remained at rest above or below, Mr Davy found its specific gravity to be to that of water, nearly as nine to ten, or more accurately as .9348 to 1.

Sodium has a much higher point of fusion than potassium; its parts begin to lose their cohesion at about 120° Fahrenheit, and it is a perfect fluid at about 180°, so that it readily fuses under boiling naphtha; it is also less volatile; it remains fixed in a state of ignition at the point of fusion of plate glass.

When sodium is exposed to the atmosphere, it immediately tarnishes, and by degrees becomes covered with a white crust, which deliquesces much more slowly than the substance which forms on the basis of potassa. This crust is pure soda.

The basis of soda combines with oxygen slowly, and without any luminous appearance, at common temperatures; and when heated, this combination becomes more rapid; but no light is emitted till it has acquired a temperature nearly that of ignition. The flame that it produces in oxygen gas is white, and it sends forth bright sparks, occasioning a very beautiful effect; in common air, it burns with light of the colour of that produced during the combustion of charcoal, but much brighter.

When thrown upon water, it produces a violent effervescence, with a loud hissing noise; it combines with the oxygen of the water to form soda, which is dissolved, and its hydrogen is disengaged. In this operation there is no luminous appearance; but when it is thrown into hot water, the decomposition is more violent, and in this case a few scintillations are observed at the surface of the fluid; owing to small particles of the base, which are thrown out of the water sufficiently heated, to burn in passing through the atmosphere. And when a globule is brought in contact with a small particle of water, or with moistened paper, the heat produced (there being no medium to carry it off rapidly) is usually sufficient for the accension of the sodium.

The base of soda, when thrown upon the strong acids, acts upon them with great energy. When nitrous acid is employed, a vivid inflammation is produced; with muriatic and sulphuric acid, there is much heat generated, but no light. When plunged beneath the surface of the acids, it is rapidly oxygenated; soda is produced, and combines with the acid.

Sodium, in its degrees of oxidation, has precisely similar habits with the base of potassa. When it is fused with dry soda, in certain quantities, there is a division of oxygen between the alkali and the base; and a deep brown fluid is produced, which becomes a dark grey solid on cooling, and which attracts oxygen from the air, or which decomposes water, and becomes soda.

The same body is often formed in the analytical processes of decomposition, and it is generated when the basis of soda is fused in tubes of the purest plate glass.

Sodium, when heated in hydrogen gas, does not, like potassium, appear to be dissolved; and as no luminous appearance attends the oxidation of it in cold water, it does not appear to be capable of combining even with nascent hydrogen.

There is scarcely any difference in the visible phenomena of the agencies of the base of soda, and that of potassa on sulphur, phosphorus, and the metals.

It combines with sulphur in close vessels filled with the vapour of naphtha with great vividness, with light, heat, and often with explosion from the vaporization of a portion of sulphur, and the disengagement of sulphuretted hydrogen gas. The sulphuretted base of soda is of a deep grey colour. The phosphuret has the appearance of lead, and forms phosphate of soda by exposure to air, or by combustion.

Sodium combines with the metals. In the quantity of $\frac{1}{40}$, it renders mercury a fixed solid of the colour of silver, and the combination is attended with a considerable degree of heat. It makes an alloy with tin, without changing its colour, and it acts upon lead and gold when heated. In its state of alloy it is soon converted into soda by exposure to air, or by the action of water, which it decomposes with the evolution of hydrogen. The amalgam of mercury and sodium seems to form triple compounds with other metals. It likewise combines with sulphur, and forms a triple compound of a dark grey colour.

If potassium be regarded as a metal, the same conclusion must be formed with regard to sodium; since it is even heavier, is less fusible and volatile, and more malleable. Nor can this conclusion well be rejected, when its general properties are considered.

Soda. After the account of the base of this alkali, I have to deliver the chemical history of the alkali itself.

It exists in the mineral kingdom in various states of combination, from some of which, particularly from the muriate and carbonate, it may be extracted. It is generally obtained, however, from the combustion of marine vegetables. In different countries, different plants are burned for this purpose. In the north of Scotland the different kinds of fuci, or sea-weed, are employed, and furnish, by a very rude process, an impure alkali named Kelp. The sea-weeds being dried, are burnt in pits dug in the sand, or on the surface surrounded with loose stone, forming what is called a kiln; fresh quantities being added, and the whole being frequently stirred until it become semi-fluid; this when cold forms hard masses *. In France and Spain the salsola, salicornia, and several others, are cultivated for this purpose. The plants are collected when in maturity, and are dried by exposure to the sun; they are then put into heaps in pits, and burned slowly †; the saline matter obtained by this process is named Barilla; it contains much more alkali than the kelp. The following is the outline of the process as it is conducted at Alicant. The plants cultivated for the purpose, the *salsola sativa*, and *salsola soda*, are pulled up in autumn and left to dry in heaps. When dried they are burnt. "Spherical holes, capable of containing about thirty hundred weight of soda, are made in the earth; above each cavity are placed two bars of iron, which support the plants to be burnt, and which are mixed with reeds or straw. Care is taken to make choice of a day when the wind is not too strong, otherwise the soda would burn too rapidly, and be reduced with more difficulty to a solid mass; it is necessary also that the air should not be entirely calm; for in that case the smoke, by not being carried off, dirties the soda. The barilla in burning experiences a kind of fusion, and is reduced to a red mass, which resembles a fused metal, and which is stirred once or twice, in order that the fusion should be more complete. When the pits are full, which generally requires a whole night, the matter is covered with earth, and it is suffered to cool for ten or twelve days; the cake formed is then uncovered *."

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* Jameson's Mineralogy of the Scottish Isles, vol. ii. 245.

† Annales de Chimie, xlix. p. 275.

The saline matter from the combustion of sea-plants is of a black or bluish colour, from the presence of charcoal and oxide of iron, and when perfectly dry is often covered with a white efflorescence of carbonate of soda; it is in masses which are hard and of a heterogeneous texture. Barilla has been analyzed by Mr Kirwan. He gives the products from one pound of the best quality in the following proportions: Carbonic acid, 960 grains; charcoal, 861.8; lime, 542.8; magnesia, 127; argil, 131.2; silex, 249.5; SODA PURE, 842; SODA IMPURE, 250; SODA mixed with common salt, 127; sulphate of soda, 125; muriate of soda, 70; earth deposited, 20 †. From this it appears, that the quantity of alkali contained in the best barilla is not considerable. Chaptal has also analyzed different varieties of it, and found the proportion of carbonate of soda to be from less than 1 to 7 oz. in one lb. with muriate of soda, sulphate of potassa, and sulphate of magnesia ‡. Mr Jameson found that, while the barilla of Alicant contained in 100 lbs. 23½ of alkali; the quantity in different varieties of the kelp of Scotland was not more than from 2½ to 5 lbs ||.

The origin of the soda afforded by the combustion of these plants is not well ascertained. The same question

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* Philosophical Magazine, vol. xiii. p. 89.

† Transactions of the Irish Academy, 1789, p. 12.

‡ Annales de Chimie, tom. xlix. p. 279.

|| Mineralogy of the Scottish Isles, vol. ii. p. 248.

may be put with regard to it as with regard to potassa. Does it pre-exist in the vegetable, or does its base exist as an element in the composition of the vegetable matter, and is oxidated during the combustion ? This appears to be answered by Vauquelin's analysis of the principal plant that affords it, the salsola soda. Its infusion in cold water afforded by evaporation two salts, having soda for their base, muriate and carbonate of soda, and the residuum of its distillation in close vessels gave similar salts ; combustion, therefore, Vauquelin concludes, serves merely to develope the saline matter in the plant, by consuming its other principles *.

Besides this, some chemists have conceived, that, supposing the soda to pre-exist in the plant, it may exist in it under the form of muriate of soda, derived from the sea-water, with which from its situation it is supplied ; that the plant by combustion may, in common with other vegetables, afford potassa, which will decompose the muriate of soda at least in part, and that the soda thus separated receives carbonic acid from the burning of the charcoal, and hence the carbonate of soda that is furnished. To this supposition, the results of Vauquelin's analyses are also so far unfavourable, as they shew that a portion of carbonate of soda exists ready formed in the vegetable. They prove also, however, that it contains muriate of soda ; and as the analysis does not prove whether the same quantity of carbonate of soda can be extracted by other processes as by burning, it is not impossible but that by the combustion the quantity of carbonate of soda may be

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* Annales de Chimie, tom. xviii. p. 65.

increased by a decomposition of part of the muriate of soda. The latter salt is evidently not entirely decomposed, as a quantity of it is always found in barilla.

That marine plants derive the soda they afford, from their situation, conveying to them muriate of soda, which is in part decomposed by the process of vegetation, and converted into carbonate of soda, appears to be proved by several experiments. Du Hamel, long ago, planted those vegetables in an inland situation, burnt them, and collected the ashes, continuing the experiment for a number of years: Cadet, examining the saline matter afforded from these ashes, found, that, in the quantity which had been produced the first year, soda predominated; in the succeeding years, the production of potassa appeared to have augmented rapidly, and at length it alone was produced *.

The soda is extracted from the impurities with which it is mixed in barilla, by lixiviation with boiling water. The solution is filtered, and exposed to the air when evaporated; it affords crystals which consist of soda combined with carbonic acid, from 3 to 5 ounces of this crystallized carbonate of soda being procured from 1 lb. of barilla. Being crystallized, it contains less foreign matter than the carbonate of potassa, which is extracted by a similar operation from the potash of commerce.

Various attempts have been made to extract soda from sea-salt, of which it is the base; and some have so far succeeded as to have been carried on, on a large scale. These are afterwards to be described.

To obtain pure soda, carbonate of soda is to be mixed

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* Mémoires de l'Acad. des Sciences, 1782, p. 146.

with an equal weight of quicklime, which being slaked by the addition of a little water, as much water is to be added as will bring the whole to a thin consistence. The mixture is put into a funnel, the neck of which is obstructed with a piece of linen, and water added as the filtration proceeds, until 5 or 6 times the weight of the carbonate of soda used has passed through. The lime attracts the carbonic acid, and the soda is dissolved by the water. Though not so impure as the potassa obtained by the same process from the carbonate of potassa, it is not in a state of perfect purity, and therefore to obtain it in this state, the process of Berthollet must be followed; the solution of soda being evaporated to the consistence of honey, alkohol being added, and the other steps followed which have already been described in the history of potassa. Berthollet has remarked, that this process does not answer so well with soda, the separation of the solution in alkohol into two portions, one holding the pure soda, the other the carbonate of soda and other salts in solution, taking place only towards the end of the evaporation; and even then it does not appear to be complete. The soda, when this process was followed by Berthollet, was obtained very confusedly crystallized.

Soda perfectly purified is in a solid white mass, which is capable of crystallization, though with difficulty, from its solution in water or alkohol; the form of its crystals is prismatic, but not very regular, and not easily determined. It is extremely acrid and caustic, has a strong attraction to water, is fused and volatilized by heat: It changes the vegetable colours to a green, neutralizes the acids, unites with oil so as to form soap, combines by fusion with silex, in one proportion forming glass, in another a compound soluble in water. It is not acted on by oxygen, nitrogen, or hydrogen; but it unites with sulphur and phosphorus.

In its physical and more obvious chemical properties, soda, it thus appears, is very similar to potassa, nor by these properties would it be easy to distinguish them, or prove that they were different kinds of matter. Soda has been supposed to be rather more fusible than potassa, and to have rather a weaker attraction to water, so as not to pass into solution on exposure to the air. They are easily distinguished, however, in their combinations. The salts which soda forms with acids, are entirely different from those of which potassa is the base. Though soda saturates a larger portion of acids in general than potassa, its salts are decomposed, at least partially, by potassa.

Soda is applied to the same purposes in the arts as potassa, and in general is preferred to the potassa.

Soda, combined with carbonic acid, is found native, forming a mineral production which is afterwards to be described. It is also a principle in several earthy fossils. Dr Kennedy discovered it in lava, and in different varieties of trap and grünstein. In the chryolite of Greenland Klaproth found it to be present in the proportion of 36 in 100. It exists in the mineral waters of Carlsbad in Bohemia, and of the Geyser fountain in Iceland, and, combined with muriatic acid, it exists in immense quantity, not only in salt springs and the water of the ocean, but in extensive strata in the earth.

BOOK IV.

OF EARTHS AND THEIR BASES.

IN common language the term Earth is applied to any substance which is solid, opaque, insipid, of a loose texture, a moderate specific gravity, uninflammable, infusible, and of sparing solubility in water. In mineralogy it is understood nearly in the same sense. But in chemical language a more appropriate signification has been attached to it. It is applied to a few bodies supposed to be simple, and at least homogeneous, which, by their mutual combinations, or mixtures, form those substances which in popular language are classed together as earths or stones. It is by analysing these that chemists have arrived at the knowledge of the earths; they remain as the ultimate principles of the analysis, and, in conformity to the principles of chemical arrangement, they were regarded as simple substances. As a natural order they were distinguished by the general properties above enumerated.

Four earths were known to the older chemists, silex, argil, magnesia and lime. Barytes and strontites were afterwards discovered; and within these few years zircon, glucine and ittria have been made known. The three last exist in nature in very sparing quantity; and the first four are the principal ingredients in the immense varieties of earthy minerals.

The substances ranked as pure earths have, in many of their properties, a strict analogy with metallic oxides. Both have similar external qualities; they are nearly of the same specific gravity, are of difficult fusibility, and sparing solubility in water, and they have relations somewhat similar both to the alkalis and the acids. From these analogies the earths were often supposed to be metals saturated with oxygen, and attempts were made to reduce them to the metallic state, which at one time appeared to be successful; metallic grains having been obtained in a series of experiments by Tondi and Ruprecht, by exposing, to intense heats, barytes, lime, and magnesia, in mixture with charcoal, the mixture being covered with calcined bones *. Klaproth, Savaresi, and other chemists, however, proved that these metallic grains were phosphuret of iron, derived from the charcoal, the matter of the crucible, and the calcined bones †. At a later period experiments were stated by Desormes and Guyton, from which they concluded that the earths are compounds, containing hydrogen and nitrogen ‡; but Darracq shewed that the results which favoured his conclusion had arisen from impurities in the substances operated on ||.

Mr Davy having effected the decomposition of the fixed alkalis by galvanism, submitted the earths to the same

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* Crell's Chemical Journal, vol. i.

† Annales de Chimie, tom. x. p. 254. 275.

‡ Mémoires de l'Institut National, tom. iii.

|| Philosophical Magazine, vol. xi. p. 311.

powerful instrument of analysis. The results, however, were much less distinct; the earths, like the alkalis, are non-conductors of electricity, and being infusible, and not easily acted on by water, they could not be rendered conductors by the same methods as those which had succeeded with the alkalis. Hence, although in submitting them to galvanic action, some changes were produced on them, and even small parts having metallic lustre were produced, yet the effect was comparatively indistinct. By submitting them to the action of the galvanic wire in mixture with potassa, or with certain metallic oxides, the results were less ambiguous, alloys being obtained, which evidently contained matter derived from the decomposition of the earths. But a method employed by Berzelius and Pontin succeeded still better. It consisted in negatively electrifying, by the galvanic apparatus, quicksilver, in contact with the earths: these chemists had thus decomposed barytes and lime, and obtained their bases in combination with the quicksilver. Mr Davy repeated the experiment with success; by the same method, he decomposed strontites and magnesia; and he succeeded in separating the quicksilver by distillation, and obtaining the bases in an insulated state. With silex, argil, zircon, and glucine, the success was much less perfect, or rather they appeared to suffer little or no change; but in submitting them to the action of galvanism, combined with potassa and soda in fusion, appearances were obtained which indicated their decomposition, and the production of bases of a metallic nature. There can remain, therefore, little doubt, that all the earths are compounds of bases somewhat analogous to those of the fixed alkalis: the alkaline earths have been fully decomposed; and, by more powerful galvanic action, or new modes of conducting the experiment, the analysis of the others will probably soon be rendered perfect.

From the results of these experiments, the earths are, perhaps, strictly speaking, to be considered as metallic oxides; and if their bases were pure, in the state in which they were obtained by Mr Davy, they approach even more nearly to the common metals than the bases of the alkalis do, as they appear to have a greater degree of density. Yet there are grounds also, as has been already stated, for considering them as a natural order, different from metallic oxides; and it is as earths that they are of most importance in the present state of the science. Under this point of view, the distinctive characters which belong to them, as well as certain general properties they possess, require to be pointed out, before proceeding to their individual history.

Of these properties, the total want of inflammability has been regarded as one of the most characteristic: this, however, is now to be regarded as arising from their being substances already saturated with oxygen. Though uninflammable, it was affirmed a few years ago by Humboldt, and the assertion was supported by some other chemists, that several of the earths absorb oxygen when exposed in a humid state to atmospheric air *. But it was demonstrated by Saussure *junior*, Chaptal and others, that there is no such absorption by the pure earths, nor any affinity exerted by them to oxygen †.

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* Journal de Physique, tom. xlviii. p. 132.

† Nicholson's Journal, 4to, vol. iv. p. 373.

The earths are of very difficult fusibility; nearly all of them requiring a very intense heat for their fusion, and some of them resisting the strongest heat that has been applied; silex and argil remain unmelted in the intense heat of the most powerful burning mirror, and lime and magnesia are not fully melted in the more intense heat excited by the united stream of oxygen and hydrogen gases kindled. When mixed with each other they are more fusible; the one promoting the fusion of the other by the mutual affinities which they exert, and the formation of a more fusible compound.

The earths are likewise in general very sparingly soluble in water. Magnesia, argil, and silex, are not dissolved in any appreciable quantity. Lime, however, dissolves in 500 times its weight of water, strontites in less than in 200, and barytes in 25 parts. These three earths, when in a dry state, attract water with considerable force, and enter into intimate combination with it, by which their cohesion is destroyed, and they are reduced to the state of a powder.

All the pure earths are capable of combining with the acids, and the greater number of them neutralize the acid properties. One of them, silex, unites with only a few of the acids, principally with the fluoric, and in small quantity with the phosphoric, boracic, and muriatic; and with these, even scarcely produces the state of neutralization. But with regard to the others, there is no such limitation. The compounds of the acids with the earths are similar, in general, in their properties, to the compounds of the acids with the alkalis. The properties of the acid and the base are completely neutralized when the substances are united in a certain proportion. Many of their salts are soluble and crystallizable; others are of sparing solubility. The affinities of some of these earths, particularly of barytes and strontites, to the acids, have been supposed superior to the affinities of the alkalis to the acids, as these earths decompose a number of the salts which the alkalis form. But, according to Berthollet, this is owing to the insolubility of the compounds of those earths with the acids, the salts of which they decompose; the force of cohesion exerted relative to the solvent, and not the superior affinity, determining the decomposition, as, in the consideration of the doctrines of chemical attraction, has been amply explained.

One chemical character has been assigned, as distinguishing the earths in their combinations with the acids, and particularly characterizing them from the metals:—that their solutions are not precipitated by the prussic acid, or the prussiates. To this, however, there are exceptions, in ittria, and, according to Klaproth, in zircon; these earths affording precipitates with prussiate of potassa. In general, their solutions are not altered by the infusion of galls, and their salts are not coloured. The only exception to this last property is in the salts of ittria, several of these having a red colour, and from this property, as well as from being precipitated by prussiate of potassa, ittria ought probably to be regarded as a metallic oxide.

Several of the earths are capable of combining with the primary inflammables, or at least with sulphur and phosphorus.

The earths and the alkalis have mutual affinities. By fusion, the two fixed alkalis combine with the greater number of the earths, and form vitrifiable compounds. And, in the humid way, potassa and soda dissolve argil, glucine, and silex, in considerable quantity. Liquid ammonia dissolves even a small portion of argil, and perhaps also of lime.

The earths and the metallic oxides are also capable of combining with each other; and some of the oxides, those of lead for example, promote greatly the fusion of the earths. By these combinations, coloured glasses are generally formed, and metallic oxides are employed in the composition of glass and enamel, on account of the colours they communicate, and the density they give to the compound. It appears that the affinities of earths and metallic oxides are also exerted in the humid way. The effect of oxide of iron in promoting the consolidation of earthy particles, in a soft or humid state, has been long known; lime can even render soluble in water the oxides of mercury, of lead, and perhaps of some other metals; and barytes and strontites, in decomposing some of the metallic salts, if added in excess, re-dissolve the oxide, which at the first addition they precipitate.

The earths have also affinities to each other. It has been long known, that, by fusion, many of them combine together, forming vitreous compounds, transparent or opaque; and that in consequence of their mutual affinities two earths mixed together generally melt at a heat inferior to that which would be necessary to fuse either of them. Some facts had also been observed, which proved the exertion of affinities between the earths in the humid way; such as the gradual induration of various earths, particularly of lime and silex when mixed together in a humid state. Scheele observed even, that in precipitating argil from its solutions by lime, if an excess of lime be added, the precipitate is re-dissolved, and forms a gelatinous substance; and Vauquelin found, that argil is capable of combining both with barytes and strontites, when it is boiled with them in water. This was a few years ago made the subject of a series of experiments by Guyton [*]; and although some of the results he obtained, appear, from the subsequent researches of Darracq [†], to have arisen from the impurity of the substances on which he operated, a number of important facts, confirmed even by Darracq's experiments with regard to the mutual affinities of the earths in the humid way, and the singular changes produced in the affinities they exert to other substances by their combination, were established. Thus, if the solution of silex in potash, and the solution of argil in the same alkali, be mixed together, a copious gelatinous precipitate is soon formed, consisting of the two earths in combination; and, what is singular, though the silex alone is soluble in scarcely any of the acids, it is by this combination with argil rendered soluble in the weakest of them, as for example in distilled vinegar. Lime-water mixed with a solution of silex in liquid potassa, forms a precipitate from the union of the two earths; and a similar effect results from adding to the same solution of silex, a solution of barytes, or of strontites in water. When the earths are dissolved in acids, the affinities exerted by the acids to them seem to be too powerful to admit of the mutual affinities of the earths bringing them into combination, so at least as to separate them from the solvent; for although some separations of this kind appeared to be established by Guyton's experiments, they were not found to take place by Darracq, when he employed the solutions perfectly pure. According to Guyton, if two earths be precipitated together from their solution, as argil and magnesia from their solution in muriatic acid, by an alkali, they unite and modify the properties of each other. The effects resulting from the affinities of earths to each other, have perhaps not been sufficiently attended to in mineral analysis.

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[*] Nicholson's Journal, 4to, vol. iii. p. 419.

[†] Philosophical Magazine, vol. xi. p. 341.

The affinities exerted by the earths to each other, to the metallic oxides, and the fixed alkalis, are also well demonstrated by the numerous combinations of this kind existing in nature.

Several of the earths have the characteristic properties of the alkalis. They are soluble in water; have much acrimony; change the vegetable colours to a green; combine with oils; precipitate metallic oxides from their solutions, and exert powerful affinities to the acids. These properties are conspicuous in barytes, strontites, and lime: they have hence been denominated Alkaline Earths, and Vauquelin and Fourcroy have arranged barytes and strontites with the alkalis. It has already been remarked, in considering this arrangement, that the alkalis and earths form a connected series, in which there is a gradation, from the two extreme substances, ammonia and silex, so that wherever the division into two orders is established, there will remain some ambiguity, or the substances commencing each order will have common properties. Of the properties above enumerated, the greater number are not peculiar to the alkalis and these two earths, but are also possessed by lime, magnesia, argil, and even by some of the metallic oxides. The connection of barytes and strontites is on the whole still more complete with lime, which is on the other side connected with magnesia, than it is with the alkalis; and their more sparing solubility in water, their insolubility in alkohol, their much greater infusibility, and the general nature of their relations to the acids, particularly in forming with the greater number of them insoluble salts, rather determine their classification among the earths. They form, however, the transition from the one order to the other, and their history is therefore first to be delivered.

CHAP. I.

OF BARYTES AND ITS BASE.

WE are indebted to Gahn and Scheele for the discovery of this earth. Scheele observed it in the course of his experiments on the native black oxide of manganese, in some varieties of which it appears to exist; and Gahn proved, that the fossil which had been known to mineralogists under the name of Heavy Spar consists of this earth, in combination with sulphuric acid. From the great weight of the native production from which it is obtained, as well as from its own superior specific gravity, it was at first named Terra Ponderosa,—a name changed by Kirwan to that of Barytes, by which it is now known.

Barytes forms a component part of but few fossils. The only native combinations of it, indeed, in which it is contained in any considerable quantity, are those in which it is combined with sulphuric acid, and carbonic acid. From either of these it may be procured.

It may be obtained from the carbonate, by exposure to the heat of a forge in a black-lead crucible, as Dr Hope first pointed out *. The addition of a little charcoal to it, considerably facilitates the expulsion of the carbonic acid, probably by converting it into carbonic oxide. By washing the residual matter with water, the pure barytes is dissolved, and may be obtained in a crystallized state.

To obtain it from the sulphate, any quantity of this fossil reduced to powder is mixed with one-third its weight of charcoal, and exposed in a covered crucible to a red heat for two hours. The sulphuric acid of the sulphate is decomposed; its oxygen being attracted by the charcoal, the sulphur remains combined with the barytes. Water is poured on the materials when they are cold, and boiled on them for a short time: the sulphuret of barytes is dissolved, and remains in solution, with a portion of hydro-sulphuret of barytes that is also formed. The barytes may be precipitated from this in the state of carbonate, by the addition of an alkaline carbonate; and this dried, may be decomposed in the same way as the native carbonate. Or, according to a process given by Vauquelin, which is preferable, diluted nitric acid may be added

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* Edinburgh Philosophical Transactions, vol. iv. p. 34.

to the liquor obtained by washing the sulphuret of barytes in water, the acid being added as long as there is any precipitation of sulphur, or disengagement of sulphuretted hydrogen : the solution is again filtered, and the nitrate of barytes which it contains is obtained in a crystallized state, and is decomposed by exposure to a red heat in a platina crucible *. The nitrate for this purpose, may also be formed by dissolving the native carbonate in diluted nitric acid.

Besides the general analogy which exists between the earths and metallic oxides, there were observed in barytes some properties which were supposed more peculiarly to denote it to be of a metallic nature; such were the great specific gravity of some of its saline combinations; sulphate of barytes, for example, being the heaviest fossil, not evidently metallic, known to exist; and also its poisonous quality. The attempts, however, to reduce it to the metallic form were equally unsuccessful with those made on the other earths.

Mr Davy, by placing barytes, slightly moistened, either alone, or mixed with potassa, in the galvanic circuit, obtained indistinct appearances of metallization; but the complete reduction was best obtained, as has been already remarked, in a mode of experiment performed by Berzelius and Pontin, negatively electrifying the earth in contact with quicksilver. On repeating this experiment with a powerful galvanic battery, Mr Davy found, that the mercury became less fluid ;—on exposing this amalgam to the air, it was covered with a film of barytes; and when

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* Nicholson's Journal, 4to, vol. i. p. 535.

thrown into water, hydrogen was disengaged, and barytes formed; a similar result was obtained from some of the saline combinations of barytes, as the muriate.

Mr Davy having found that the presence of oxide of mercury favoured the decomposition of barytes, combined this method with that of the Swedish Chemists. The earth slightly moistened, and mixed with one-third of red oxide of mercury, was placed on a plate of platina, having a cavity to receive a globule of mercury; the whole was covered by a film of naphtha, and the plate was made positive, the mercury negative, by communication with a very powerful galvanic battery. An amalgam was obtained; and to procure from this the base of the barytes it was distilled in a tube of glass, bent in the middle, and enlarged, and rendered globular at each extremity, so as to form a kind of retort and receiver; a little naphtha too having been introduced into the tube, and boiled, so as to exclude the air. The quicksilver rose pure by distillation, but it was very difficult to obtain a complete decomposition, a red heat being required for this, and at this heat the base of the earth acting on the glass. The result therefore was less perfect than those with regard to the bases of the alkalis; and there remained the uncertainty but that the metallic base procured might have retained in combination a little quicksilver. To the metallic matter obtained from barytes, Mr Davy has given the name of Barium. Barytum would perhaps better denote its relation to the earth, according to its established name.

Barium or barytum, as obtained by the experiment above described, appeared as a white metal of the colour of silver. It was fixed at all common temperatures, but became fluid at a heat below redness, and did not rise in vapour when heated to redness in a tube of glass. It acted, however, violently on the glass, producing a black mass, which seemed to contain barytes and a fixed alkaline base in the first degree of oxygenation. When exposed to air, it rapidly tarnished, and fell into a white powder, which was barytes; and when this process was conducted in a small portion of air, oxygen was absorbed. When the base was dropt into water, it acted on it with great violence, sunk to the bottom, producing barytes, and generating hydrogen gas. It not only sunk in water, but even in sulphuric acid, though surrounded by globules of hydrogen; hence Mr Davy concluded that it cannot be less than four or five times heavier than water. Whether it owe this in part to a little mercury combined with it is uncertain. It flattened by pressure, but required for this purpose a considerable force.

Mr Davy endeavoured to ascertain the proportions of base and of oxygen in the composition of barytes, but without success. He ascertained, however, that when burned in a small quantity of air, it absorbed oxygen, gained weight in the process, and the earth produced was in the driest state. The conclusion follows, therefore, that Barytes is a compound of this base with oxygen.

Barytes, in the state in which it is obtained by the operation already described, the decomposition, by heat, of the compound it forms with nitric acid, is in the form of a grey, solid, and somewhat porous mass. Its taste is harsh and caustic, even more so than that of lime; and it destroys the texture of animal matter. It is the only earth which is poisonous to animals. From exposure to the air, it splits, falls to pieces, and at length passes to the state of a white powder, in consequence of the absorption of water,—an operation analogous to the slaking of lime. It thus increases in weight, according to Vauquelin, to the extent of 0.22, from the absorption of water and carbonic acid.

There is some doubt with regard to the fusibility of barytes. As obtained by the decomposition of the nitrate, it fuses, as Vauquelin has remarked, when exposed on charcoal to the flame of the blowpipe, and runs into globules, which penetrate the charcoal; and, according to Fourcroy, on being put into a crucible of porcelain which has been made red hot, it melts, and adheres to the sides of the vessel, forming a kind of greenish coating. It appears, however, that these are examples of its aqueous fusion, and that, when the water is dissipated, it is much less fusible. Fourcroy has remarked, that if it be gradually heated, it rather hardens. Saussure had before observed, that it suffered a kind of fusion, by which it is converted into a spongy substance, at a temperature which he estimated at 31° of Wedgwood, while, at a much higher temperature, which he estimated at 58° of the same scale, it was more perfectly melted, so as to form a translucid globule *. Lavoisier found it to melt in the heat excited

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* Journal de Physique, 1795.—From the method in which Saussure estimated the temperatures, in his experiments on the fusibilities of different substances by the heat excited by oxygen gas, they are all stated considerably too high.

by oxygen gas; but the earth on which he operated appears to have contained a little sulphuric acid, by the sulphur of which its fusibility might be promoted; and when pure, he states it to be infusible*. Guyton, however, more lately found it to melt by this heat †; and he must probably have employed it in a state of purity, as the method of obtaining it in such a state is better known than at the period when the experiments of Lavoisier were made: and Mr Hare found it likewise to melt, exposed, either on a support of charcoal or of silver, to the kindled flame of oxygen and hydrogen gases ‡. It appears, on the whole, that barytes is fusible, but that its real fusion requires a very high temperature.

Barytes is soluble in water, and since the method of obtaining it in a state of purity has been discovered, its solubility is found to be much greater than had formerly been supposed. This, as well as the crystallization of this earth, was first observed by Dr Hope in his researches on strontites. The porous mass, obtained by the decomposition of the nitrate by heat, absorbs water with great avidity, and an elevation of temperature: it hardens; but the addition of a little more water changes it into a white powder; if at once covered with water it dissolves in it, and forms a congeries of transparent needle-like crystals. Cold water dissolves, according to Vauquelin, who has observed these effects, a twenty-fifth part of its weight: boiling water more than one-half: the latter solution deposites, on cooling, transparent prismatic crystals, which effloresce and fall to powder, when exposed to the air *. These crystals are described by Dr Hope as being, when well formed, flat six-sided prisms acuminated by four planes. When heated, they undergo the watery fusion, and, as the heat is continued, the water is dissipated, and leaves the barytes in a white powder. Dr Hope found the crystallized barytes to be soluble in 17.5 of water, at the temperature of 60 †.

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* Mémoires de l'Acad. des Sciences, 1783, p. 588.

† Journal de l'Ecole Polytech. Cah. III. p. 300.

‡ Philosophical Magazine, vol. xiv. p. 301.

The solution of barytes in water has an acrid taste: it changes the vegetable colours to a green. Exposed to the atmosphere, it absorbs carbonic acid more quickly than lime-water, a pellicle sooner appearing on its surface.

According to Vauquelin, it is soluble in alkohol, though other chemists have denied to it this property.

Barytes combines with the acids, and has been supposed to exert to them a more powerful attraction than the alkalis, or any of the other earths, as it decomposes all their neutral salts, or abstracts the acids from every other base. This, however, according to the doctrine of Berthollet, already explained, is owing to the great insolubility of the salts of barytes; and this apparent superior attraction is to be observed only in relation to those acids with which it forms insoluble compounds. With regard to those with which it forms soluble salts, as, for example, muriatic or nitric acid, the experiments of Anfrye and Darcet have shewn, that no such superiority in the force of the affinity exerted by barytes exists, as it merely

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* Nicholson's Journal, 4to, vol. i. p. 537.

† Edinburgh Philosophical Transactions, vol. iv. p. 38.

produces partial decompositions of the salts of these acids, and the alkalis precipitate it from the salts it forms with them *. In the power of neutralizing the acid properties, it is inferior to almost all the other bases. Its combinations with the different acids are to be afterwards considered.

Barytes appears to exert no marked action on the alkalis, though with the fixed alkalis it may be fused into a species of frit. With borax or phosphate of soda, it forms a transparent glass.

Barytes exerts affinities to several of the other earths. It has the power even of communicating solubility to those of them that are least soluble. Thus by fusion with silex, a compound is formed which is soluble in all the acids, even the weakest; and when barytes and argil, in equal parts, are boiled in water together, both of them are dissolved; or, if a saturated solution of barytes be poured into muriate of argil, a precipitate is formed, which consists of the two earths in combination, and which is redissolved when an excess of barytes is added. These facts were ascertained by Vauquelin †. The precipitation of argil from muriatic acid, however, by barytes, has been affirmed by Darracq and Chenevix not to take place. Barytes precipitates silex from its alkaline solution, by uniting with it. It appears to exert no affinities in the humid way to lime, or to magnesia. And even by fusion it does not appear to enter into combination with them, or with argil, at least mixtures of them do not fuse in the most intense heat. Barytes and silex fuse in various propor-

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* Annales de Chimie, tom. xlix. p. 95. Nicholson's Journal, vol. xviii. p. 68.

† Nicholson's Journal, 4to, vol. iii. p. 123.

tions, and form a green glass or enamel. Ternary mixtures of these earths are more fusible *.

Barytes combines with sulphur by fusion, and when they are boiled together in water, the barytes causes part of the sulphur to be dissolved, and on cooling, hydro-sulphuret of barytes crystallizes. It unites, too, with phosphorus, when the combination is promoted by heat. It acts on none of the metals, but unites with some of the metallic oxides by fusion; and, even in the humid way, Vauquelin having remarked, that when barytic water is added to solutions of nitrate of silver or lead, so as to precipitate the oxide, this precipitate is re-dissolved, on adding a new portion of barytic water.

A peculiar chemical character has been assigned to barytes,—that the solutions of its salts afford a precipitate with the alkaline prussiates; and this was regarded as in some measure even assimilating it with the metals, the solutions of which are so generally precipitated by this test. Meyer and Klaproth observed, however, that no such precipitation from the solutions of barytes takes place, unless when the prussiate employed is contaminated with a sulphate from which it is difficult to obtain it free †. Mr Henry shewed, that although no immediate precipitate is formed, on the addition of prussiate of potassa to a barytic salt, when the prussiate is pure, yet in a few hours crystals are deposited from the liquor, consisting of prussiate of barytes; which proves, that the salts have, in part at

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* Kirwan's Mineralogy, vol. i. p. 57, &c.

† Analytical Essays, vol. i. p. 393.

least, exchanged their principles [*]: but this, as Guyton has remarked, is not peculiar to this earth; a similar exchange happening with the salts of other earths and alkalis [†]. Mr Henry observes, that the same crystals are formed from barytic water added to the prussiate.

CHAP. II.

OF STRONTITES.

THE existence of this earth was discovered by Dr Hope, by whom also its distinguishing characters and principal chemical properties and combinations were ascertained. The native carbonate of it found at Strontian in Argyleshire, had been for some time known to mineralogists, but had been considered as a variety of carbonate of barytes, and this even by Pelletier, by whom it had been submitted to chemical analysis [‡]. Dr Hope, at an early period, suspected the truth of this opinion; and, in 1792, executed a series of experiments, by which it was demonstrated to contain an earth before unknown, to which, from the name of the place where it had been found, he gave the denomination of Strontites. He afterwards published a memoir on its properties and combinations in the

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[*] Nicholson's Journal, 4to, vol. iv. p. 30.

[†] Ibid. 8vo, vol. iii. p. 196.

[‡] Mémoires de Chimie, tom. i. p. 386.

4th volume of the Edinburgh Philosophical Transactions. Klaproth also, unacquainted with Dr Hope's experiments, had examined the native carbonate; and Pelletier resumed his investigation of it, and, by both these chemists, the existence of this as an earth different from every other, was established *. It has since been found native, combined with sulphuric acid.

Strontites may be obtained by processes similar to those by which barytes is procured, either from the native sulphate or carbonate. Dr Hope found, that the native carbonate is decomposed by an intense heat, as did also Klaproth, and they thus obtained strontites, separating it from any insoluble matter by the action of water. It may also be obtained by decomposing the nitrate by heat.

Mr Davy effected the decomposition of this earth by the same modes of galvanic analysis, as those applied to the other earths. By negatively electrifying it in contact with mercury, the phenomena denoting the decomposition of the earth and the addition of metallic matter to the mercury rapidly took place. And, by employing the process which has been already described under the history of barytes, the metallic base of the strontites was obtained.

STRONTIUM, as this base has been named by Mr Davy, has been very imperfectly examined. It has the general characters of the base obtained from barytes, and by exposure to the air, is again converted into strontites, absorbing oxygen, and gaining weight in the process. Like

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* Klaproth's Analytical Essays.—Mémoires de l'Instit. National, tom. i. p. 88.; or Nicholson's Journal, 4to, vol. i. p. 518.

barytum, it sinks in sulphuric acid, and is therefore of considerable specific gravity.

STRONTITES, obtained by the usual processes, has a pungent acrid taste, rather less harsh than barytes. It is not poisonous like that earth. It can be obtained in crystals. Dr Hope formed them by throwing into boiling water the recently calcined carbonate: on allowing the solution to cool, crystals of strontites were formed an inch in length; their form being a thin quadrangular table, or compressed prism, sometimes bevelled at the extremities: they are transparent, but become white and efflorescent, on exposure to the air, from the loss of their water of crystallization. They undergo the watery fusion, and, when this is expelled, remain in the state of a white powder; 100 parts losing by this operation 68 of weight. This powder is not fused by a very strong heat: the flame of the blowpipe does not affect it, further than rendering it phosphorescent.

Strontites is soluble in water, but much less so than barytes. It requires 50 parts of water at 60° for its solution, but is much more soluble in boiling water, the water dissolving nearly half its weight. The strontites not in a crystallized state, and free from water, is, of course, more sparingly soluble; it requires nearly 200 parts of water at 60°. Its solution changes the vegetable colours to a green. It is also soluble in alkohol.

This earth combines with all the acids, and exerts to them affinities which have been regarded as powerful. The salts it forms with them are in general decomposed by barytes, and several of them at least partially by the alkalis and lime: there are others, however, of the salts of these bases which strontites decomposes. A distinguishing property of its salts is, communicating a blood-red colour to the flame of combustible bodies,—a property best displayed in those which are soluble in alkohol; the alkohol, holding the salt in solution, burning with this coloured flame. Its saline combinations fall to be considered under the history of the acids.

Strontites exerts no marked action on the alkalis, nor on barytes or lime. With some of the others, particularly with silex and argil, it combines.

Strontites combines with sulphur, by exposing a mixture of equal parts of them to heat in a covered crucible. The compound is dissolved by water; the solution acquiring a yellow colour, and being, of course, a sulphuretted hydro-sulphuret. A similar compound is formed, by boiling strontites and sulphur in water. It is also capable of being combined with phosphorus by the usual process, and of forming a compound which decomposes water.

Though strontites has, in a number of its properties, a considerable resemblance to barytes, yet in others it is so totally different, as to prove it to be a substance altogether distinct. It is distinguished particularly by its less solubility; by the different form of its crystals; by the greater solubility of a number of its salts, particularly of the nitrate and muriate; by its salts being decomposed by barytes; and by the blood-red colour which they give to the flame of combustible bodies. There are two tests by which these earths may be discriminated. When the salts of strontites are precipitated by oxalic acid, the precipitate is not redissolved by an excess of acid, as that from the barytic salts is; and the watery solution of strontites is not, like that of barytes, precipitated by malic or by gallic acid.

CHAP. III.

OF LIME.

THIS earth is found in great abundance in nature: it is the principal constituent part of marble, lime-stone, plaster-stone, marl, and many other fossils. In a combined state it is contained in all spring and river water: it exists in the water of the ocean; is found in vegetables; and is the basis of the shells, bones, and other hard parts of animals. It appears to exist in these combinations, or at least in the greater number of them in the state of lime, and not in that of the metallic base, of which, combined with oxygen, it is now proved to be formed.

To obtain it in a state of purity, white marble, or the shells of marine animals, are exposed to a strong heat, sufficient to expel the carbonic acid with which the lime is combined. As thus obtained, however, it may still be combined with foreign substances: that from marine shells may have an intermixture of phosphate of lime; and even those marbles which appear most pure often contain other earths, particularly silex, with which the lime will be mixed. The lime, therefore, should be further purified by solution in an acid. The process given by Mr Chenevix to obtain pure lime, is to dissolve white marble in dilute muriatic acid, leaving an excess of lime undissolved: the solution should afford no precipitate with ammonia,—as a proof that neither argil nor magnesia is present: it is then to be decomposed by a solution of pure carbonate of potassa, and the carbonate of lime, which is thrown down, having been well washed with water, is to be exposed to a violent heat in a platina-crucible, until it cease to lose weight *.

Lime subjected to the action of galvanism in high intensity, Mr Davy found gave appearances of decomposition; when mercury was submitted along with it to this action, an amalgam was formed; and when the process already described, under the history of barytes, was applied to lime, this amalgam was readily produced. Exposed to the air, lime was regenerated; and the same effect was immediately obtained by the action of water, hydrogen being evolved, and the quicksilver remaining free.

Mr Davy has not been able to examine the properties of the base of lime in its insulated state. In the experiment in which the quicksilver had been distilled from it to the greatest extent, the tube broke while warm; "and at the moment that the air entered, the metal, which had the colour and lustre of silver, instantly took fire, and burnt with an intense white light into quicklime." To this base Mr Davy proposes to give the name of CALCIUM.

LIME when pure is perfectly white: if in a coherent mass, it is moderately hard, brittle, and having a specific gravi-

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* Memoirs of the Irish Academy, 1802.

ty of 2.3 : it has a very pungent bitter taste, and acts as a powerful caustic, destroying quickly the texture and cohesion of animal and many vegetable substances. It changes the vegetable colours to a green. According to Trommsdorff, it can be obtained in a crystallized state, by boiling four parts of a solution of muriate of lime with one part of lime ; needle-shaped crystals of lime shooting through the liquid when it is cold. These, however, are sub-muriate of lime.

Lime is infusible : if not perfectly free from the other earths, it will vitrify by a very strong heat, but, if pure, it undergoes no agglutination in the focus of the most powerful burning mirror. Lavoisier could not melt it by the heat of burning charcoal excited by oxygen gas : it appeared only to be imperfectly agglutinated, and, both in his and Guyton's trials, to form a kind of enamel on the edges when exposed in small fragments to the flame. Even in the still stronger heat excited by oxygen and hydrogen gases kindled, its fusion is doubtful : black vitreous globules were obtained from exposing it to the flame on charcoal, in Mr Hare's experiments, when the fusion might perhaps have been promoted by the earthy or metallic matter of the charcoal.

When water is poured on quicklime, a phenomenon somewhat singular presents itself. The water is absorbed with a hissing noise, the lime splits, and falls down into a fine powder, which, although it contain a quantity of water nearly equal to one-fourth its weight, is perfectly dry. And so much caloric is at the same time evolved, as to convert a portion of the water into vapour. This process is the slaking of lime : the phenomena accompanying it are owing to the strong attraction of lime for water: it attracts it until saturated with it; and as in this combination the water passes to the solid state, a large quantity of caloric is evolved. The caloric, therefore, proceeds from the water, and not, according to the vulgar opinion, from the lime. Pelletier observed, that in this operation the lime is often phosphorescent.

Lime is also slaked by exposure to the air, from which it gradually attracts a sufficient quantity of moisture.

At the temperature of 60, water dissolves completely about $\frac{1}{600}$th of its weight of lime. At 212, it takes up double this quantity, but this excess is deposited as the water cools. The solution is known by the name of Lime-Water. It is colourless and transparent; has a styptic taste; and changes several of the vegetable colours to green. On exposure to the air, its surface is soon covered with a thin pellicle, which thickens till it breaks and falls down; another is formed, and this goes on till the water become nearly tasteless. This change is owing to the lime attracting carbonic acid, and being converted into the carbonate, which is insoluble. A similar absorption of carbonic acid takes place, when lime in powder is exposed to the atmosphere, but much more slowly; and there are some facts which shew, that in a perfectly dry atmosphere there is scarcely any absorption whatever. It has even been affirmed that pure lime is to be found in nature.

Lime combines with the acids, forming compounds in which the acid properties are fully neutralized. The history of its salts belongs to that of the acids of which they are formed. They are in general decomposed by the fixed alkalis which precipitate the lime, but not by ammonia; owing, as Berthollet supposes, to the tendency of this alkali to enter into ternary combinations with the lime and the acid, —a combination which he has shewn by experiment is established *. They are also decomposed by a number of neutral salts, by complex affinity, exerted either in the humid or in the dry way.

It does not appear to exert any affinity to the alkalis in the humid way; nor does it even combine with them by fusion; a mixture of lime, with soda, remaining without aggregation, even in the heat excited in burning charcoal by a stream of oxygen gas †. It forms a transparent glass, however, by fusion with borax.

It exerts affinities to several of the other earths. With barytes or strontites it does not combine, but it unites either in the humid way, or by the aid of heat, with magnesia, argil, and silex; and to these combinations has been ascribed, in part at least, the induration of mortar. These compounds will be noticed under the history of these earths.

Lime is capable of entering into combination with the simple inflammables. Its combination with carbon is indeed doubtful; yet when exposed to an intense heat with carbonaceous matter, they form a kind of frit; and charcoal, even in its finest state of aggregation, as in lampblack, contains lime. It forms perfect combinations with sulphur and phosphorus, both at a high temperature in a dry state, and also by boiling in water.

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* Researches on Chemical Affinity, p. 100.

† Journal de l'Ecole Polytech. Cah. III. p. 302.

Lime is incapable of combining with the metals; but it promotes the oxidizement of several of them by water and air, and unites with their oxides. Thus, it melts with oxide of lead into a species of glass; and with oxide of iron it forms a coloured porcelain. In the humid way, it also combines with oxide of lead; forming a compound, which, as Berthollet has observed, is soluble in water in nearly the same proportion as lime itself, and which, by evaporation, may be obtained in small transparent crystals. According to the observation of the same chemist, lime-water, boiled on oxide of quicksilver, dissolves a portion of it, and forms a crystallizable compound *.

The uses of lime are numerous and important; and under this point of view, it may be considered as holding the same place among the earths that iron does among the metals. In the practice of agriculture, the utmost advantage is derived from it as a manure; and though part of its utility may depend on its mechanical operation on the soil, and part on its chemical agency in promoting the decomposition of vegetable and animal substances, the whole theory of its action is not yet perhaps understood. It forms the basis of all the varieties of mortar; the induration which it produces arising, in a great measure, from its gradual intimate combination with the water which is necessarily added to give the soft consistence. In practical chemistry, and in many of the chemical arts, it admits of numerous applications, from its chemical agencies, and, in particular, from its relations to the acids, the compound salts, the other earths, and many of the vegetable and animal products. In medicine, it is employed as an antacid and astringent.

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* Annales de Chimie, tom. i. p. 53—61.

CHAP. IV.

OF MAGNESIA.

HOFFMAN first distinguished this earth as different from the others. It had been before known, and employed as a medicine, but had been generally confounded with carbonate of lime, or supposed, at least, not to differ greatly from it. Hoffman observed, that it forms with sulphuric acid a salt totally different from that formed by the union of lime with the same acid. Dr Black soon afterwards undertook the investigation of its properties; and it was in this investigation that he was led to his important discovery of carbonic acid gas. He established clearly the distinction between it and lime, and shewed that it has properties different from all the other earths. Margraaf confirmed this, and its chemical relations were further investigated by Bergman.

This earth is not presented to us by nature in a state of purity. It is an ingredient, however, in many fossils; and several of the salts which it forms by combination with the acids are found in mineral springs, and in the water of the ocean. It is from these saline combinations that magnesia is obtained, by an artificial process.

The sulphate of magnesia is, in particular, used for this purpose. One part of it is dissolved in 20 of water, and the solution is filtered: there is added to it, while hot, a solution of pure potash, or soda, as long as any precipitation is produced: the alkali combines with the sulphuric acid, and the magnesia is separated: being insoluble in water, it falls down in the form of a white powder: its deposition is facilitated by boiling the liquor slightly: it is washed with water, till the fluid comes off tasteless, and is dried by a moderate heat. Sometimes the carbonate of the alkali is used for the precipitation; the carbonate of magnesia is thus obtained: and from this the carbonic acid is expelled, by exposing it to a red heat: and this is probably a preferable process for obtaining the magnesia perfectly pure, as it must thus be obtained with more certainty, free from any small quantity of sulphuric acid, which may perhaps be retained in combination with it when precipitated by the pure alkali.

Magnesia, when submitted to the action of galvanism, Mr Davy found, was less acted on than the preceding earths, probably from its insolubility and the difficulty therefore of rendering it a conductor of electricity. But by submitting to experiment, not the earth itself, but some of its saline compounds, as the sulphate or nitrate in contact with mercury, the decomposition was effected more speedily, and an amalgam obtained. From this amalgam, magnesia was reproduced by exposure to the air. Mr Davy did not succeed in expelling the whole of the quicksilver from the magnesian base, the glass of the tube being acted on before this result was obtained. In an experiment in which the process was stopt before the mercury was entirely driven off, a solid was obtained, having the same whiteness and lustre as the other metals of the earths. "It sunk rapidly in water, though surrounded by globules of gas, producing magnesia, and quickly changed in air, becoming covered with a white crust, and falling into a fine powder, which proved to be magnesia."

Mr Davy has proposed to name the base of this earth MAGNIUM. He admits, however, that it is objectionable, MAGNESIUM being that which properly denotes its relation to the earth. His reason for not adopting the latter is, that it has been applied by Bergman to metallic manganese. If the name of this metal, however, were now to be given in the Latin language, Manganesium would no doubt be used, and there can be very little hazard of any mistake, from the former acceptation of the word magnesium. It will therefore probably be applied to the base of magnesia.

MAGNESIA exists under the form of a white light and spongy powder, soft to the touch, inodorous, and impressing on the tongue a slightly bitter taste. Its specific gravity is about 2.3. It slightly changes the vegetable colours to a green.

When perfectly pure, it is infusible when exposed even to the most intense heats. In the focus of the most powerful burning mirror, or in the heat excited by a stream of oxygen gas, directed on burning charcoal, it is not melted; and even in the still more intense heat excited by the kindled stream of oxygen and hydrogen gases, its fusion is doubtful; Mr Hare having obtained only small black vitreous masses when it was exposed to the flame on charcoal, and the fusion being, therefore, promoted perhaps by some of the substances contained in the charcoal. When made into a paste with water, it contracts when exposed to a sudden heat as argil does, but not to the same extent.

This earth may be said to be nearly insoluble in water; one part of it requiring for its solution, according to Mr Kirwan's estimate, not less than 7900 times its weight. When dry, it absorbs its weight of water, but it does not form an adhesive paste, or at least one very slightly so.

Magnesia combines with facility with the acids, and forms peculiar neutral salts. The greater number of these are soluble or crystallizable, and have a very bitter taste. It has been supposed, that its attractions to the acids are inferior to the attractions of the fixed alkalis, of lime, barytes, and strontites: its salts are at least decomposed by them, and likewise partially by ammonia. The ammonia has a tendency to form with the magnesia and the acid ternary combinations; which have been named ammoniacal magnesian salts; they were first noticed by Bergman, and were afterwards more fully examined by Fourcroy *. The different magnesian salts fall to be considered under the history of the acids.

Magnesia and the alkalis exert no mutual action; nor does it appear to act powerfully on the earths. With barytes or strontites it does not combine. In the humid way it exerts no sensible attraction to lime: but they combine by fusion at 150° or 160° of Wedgwood, when the lime is in larger proportion than the magnesia; in equal parts, they do not melt at these heats. It exerts a strong attraction to argil in the humid way, and this attraction appears to be one of the strongest that one earth exerts to another. It is displayed in a singular fact, observed by Mr Chenevix in the analysis of some magnesian fossils, that although

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* Annales de Chimie, tom. iv.

magnesia cannot be precipitated entirely from any of its salts by ammonia, yet, if argil be present, its precipitation is complete. Thus, it was found, that on adding an excess of ammonia to a solution of muriate of magnesia, mixed with a large proportion of muriate of argil, nothing remained in solution but muriate of ammonia: the two earths were precipitated in combination, and the affinity of the argil to the magnesia had so much aided the decomposition, as to render it complete. And this affinity between the two earths, was even sufficient to resist the action which potassa is capable of exerting on argil *. It does not melt, however, with argil alone even at the most intense heat. Ternary mixtures of magnesia, lime, and silex, magnesia, lime, and argil, and magnesia, argil, and silex, are more fusible, forming in various proportions a porcelain, or glass, though in all these the magnesia must be in a proportion inferior to that of the other earths, to admit of the fusion of the mixture †.

No chemical action appears to be exerted between magnesia and any of the simple gases, nor between it and any of the simple inflammables, sulphur excepted. They combine, though not very intimately, when the sulphur is in fusion, or when it is boiled with the magnesia in water. Sulphuretted hydrogen transmitted through water, in which magnesia is suspended, dissolves also a small quantity of it.

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* { Annales de Chimie, tom. xxviii. p. 189.
{ Philosophical Transactions, 1802, p. 345.

† Kirwan's Mineralogy, p. 62, &c.

Magnesia has no action on the metals, nor does it appear even to combine by vitrification with the metallic oxides.

This earth is scarcely applied to any use, except that in its pure form, and in several of its saline combinations, it is employed in the practice of medicine; and some of the native compounds of it with other earths are used sometimes in the manufacture of porcelain.

CHAP. V.

OF ARGIL.

THIS earth does not exist in nature in a state of perfect purity; and, in those fossils which consist principally or almost entirely of it, the aggregation is so great, that its chemical relations can scarcely be discovered. It is therefore always prepared by an artificial process. The salt, long known by the name of Alum, consists principally of it in combination with sulphuric acid: one part of it is dissolved in 20 parts of water, and the solution being filtered, liquid ammonia is added to it as long as any precipitation is produced. The precipitate is well washed, and, when dried, has been supposed to be pure argil. It always retains, however, a little sulphuric acid combined with it: to obtain it pure, therefore, it ought to be redissolved in nitric acid, be again precipitated by ammonia, and, when dried, be exposed to a low red heat: the pure earth will thus be obtained. The existence of argil as a distinct earth, which forms the principal constituent part of the natural clays, was first fully established by Margraaf, by whom several of its properties were also determined. It is from existing as the basis of clay that its name argil has been derived. Some chemists name it alumine or alumina, a denomination more ambiguous, and having no advantage.

Mr Davy endeavoured to decompose this earth, but the methods which had usually proved successful, as well as several others, failed. That which succeeded best, consisted in submitting the argil to the galvanic action in a state of fusion with potassa, or with soda. Metallic globules were produced, consisting no doubt principally of the alkaline base; but with this there were also appearances which indicated that the argil had been decomposed: the metal, when soda had been employed, was less fusible than sodium; when acted on by water, it produced soda and a white powder; and the metallic matter obtained when the argil had been submitted to electrization with potassa, rapidly decomposed water, and afforded a solution which deposited argil by the action of an acid. By electrifying negatively under naphtha, potassium amalgamated with one-third of mercury in contact with argil, and causing the amalgam, after this had been continued for some time, to decompose water, a solution was obtained, which gave a cloudiness on the addition of an acid. These results, however, as Mr Davy states, are so imperfect, and the earth reproduced was in so minute a quantity, that the decomposition cannot be considered as established by the same evidence as that by which the decomposition of the alkalis and alkaline earths is proved.

Argil, obtained by the process above described, is in the form of a light white powder, spongy, and adhering to the tongue when applied to it: it is perfectly tasteless; is smooth and somewhat unctuous to the touch: it imbibes water, and, when kneaded with it, forms an adhesive plastic mass. It is from this earth that the natural clays derive their plastic quality. It may be easily diffused through that fluid, but is quite insoluble in it. It appears, however, to form some kind of combination with it. T. Saussure remarked [*], that the precipitate thrown down by an alkali from a solution of alum, is different in its appearance according to the quantity of water with which the solution had been diluted. If the solution be concentrated, the precipitate, when dry, is a light friable powder, which adheres to the tongue, while, if the quantity of water has been large, the precipitate dried is transparent, yellow and brittle, is not earthy in appearance, does not occupy so much volume, and does not adhere to the tongue. The former he names *spongy*, the latter gelatinous alumine; and the latter he found to retain the water contained in it much more forcibly than the other. After incandescence it still contains 0.15 of water, and argil appears therefore to have a strong affinity to water; the combination it forms with it being somewhat analogous to that in dry, or as it is named slaked barytes or lime.

The paste, formed by kneading argil with water, contracts when exposed to heat, and this even after all the water which it had imbibed has been expelled from it. The circumstances connected with this contraction, and its application to pyrometry, have been already considered, (vol. i. p. 150. 194). The clay thus heated loses its plastic power, and acquires greater hardness, so as to be capable of scratching glass, and of striking fire with steel.

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[*] Journal de Physique, tom. lii.

In the most intense heat of the most powerful burning mirror, argil is not fused. Lavoisier, however, and afterwards Guyton, found it to be melted by the heat excited by a stream of oxygen gas directed on burning charcoal: it formed a white semi-transparent enamel of great hardness *.

No chemical action is exerted between argil and oxygen, nitrogen, or hydrogen.

It unites with the acids, and is capable of completely neutralizing the acid properties. Those of its salts which are soluble are distinguished by a peculiar taste, sweetish, and at the same time strongly astringent. All its saline combinations are decomposed by the alkalis; these attracting the acid, and precipitating the argil more or less pure.

Argil has the property of combining, in the humid way, with the alkalis. When any of its salts is decomposed by an alkali, if an excess of alkali be added, the precipitate which was first formed is redissolved; a solution of the pure earth is also effected, when it is boiled in an alkaline solution. It appears, that the combination may also be effected in the dry way; for, although the mixture of argil and either of the fixed alkalis is not fused into a perfect glass, yet a species of frit is formed, and the argil is rendered soluble in water. This combination of argil with an alkali is subverted, by the addition of an acid, which saturates the alkali, and precipitates the earth.

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* Journal de l'Ecole Polytech. Cah. III. p. 299.

Argil exerts affinities to other earths, and it appears peculiarly to have relations both to these and to the alkalis. It unites with lime, barytes, strontites, magnesia, and silex, both in the humid and the dry way. Barytes, it has been already remarked, communicates solubility to it, so that when equal parts of barytes and argil are boiled in water, both are dissolved. Strontites has an effect on argil somewhat similar to that of barytes. Five parts of it boiled with one of argil, render a part of it soluble, while a portion of the strontites remains insoluble in combination with another part of the argil. Lime has likewise an attraction to argil. When argil is added to lime-water, it attracts the lime, as Scheele first observed, and an insoluble combination of the two earths is established. Mr Chenevix has remarked, that when a solution of potassa is boiled on a mixture of lime and argil, the argil is dissolved, together with a much greater portion of lime than can be attributed to the dissolving power of the water alone; while, if the alkaline solution be boiled on lime alone, no more lime is dissolved than would be by the mere water of the solution, a proof that its solubility is promoted by the argil *;—an important fact, both in a theoretical point of view, and as related to mineral analysis. These earths also combine, though with difficulty, at very intense heats. They cannot be fused in a furnace; but when the argil predominates, they are melted by the heat excited by oxygen gas. With magnesia it does not unite readily. A mixture of equal weights of these two earths, Guyton found to re-

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* Philosophical Transactions, 1802, p. 346.

main pulverulent at a heat at which the crucible began to vitrify; and Kirwan found, that in whatever proportion they were mixed, they exerted no mutual action at the most intense heat. The exertion of a mutual attraction between silex and argil, in the humid way, is shewn, in the experiment of Guyton already quoted; in which, when a solution of silicated potash, and of argil in potash, are mixed together, the two earths are precipitated in combination, by which the properties of each are modified. The same affinity is exerted in the dry way: when favoured by a very intense heat, they enter into fusion, and form a milky glass or enamel.

This combination of silex and argil is the basis of Porcelain, and, with the addition of various proportions of other earths, and even of some metallic oxides, forms the different varieties of pottery, from the finest porcelain to the coarsest earthen ware.

Though siliceous earth is the ingredient which is present in largest proportion in these compounds, yet it is the argillaceous which more particularly gives them their character, as it communicates ductility to the mixture when soft, and renders it capable of being turned into any shape on the lathe, and of being baked. The clays are native mixtures of these earths; but they are often rendered unfit for the manufacture of at least the finer kinds of porcelain, from other ingredients which they also contain: lime is almost always present in them: when it is not in larger proportion than 5 or 6 parts in 100, it does not materially injure the quality of the porcelain; but in a larger proportion, it renders the mixture too fusible: oxide of iron is also often present, and, when in any perceptible quantity, it always communicates a yellowish or red tinge.

It is obvious, therefore, that the perfection of porcelain will depend greatly on the purity of the earths of which it is composed; and hence, the purest natural clays, or those consisting of silex and argil alone, are selected. Two substances have been brought to Europe, as the materials from which the Chinese porcelain is formed,—what have been named Kaolin and Petuntse. The kaolin, according to Vauquelin, consists of silex 74, argil 16.5, lime 2, and water 7; the petuntse, of silex 74, argil 14.5, lime 5.5: the two, when mixed, therefore, consist of argil and silex, with less than 5 *per cent.* of lime. It was found difficult to procure, in Europe, natural clays equally pure, and hence, in part, the difficulty of imitating the porcelain of the East. Such clays, however, have now been discovered in different countries, and hence the superiority to which the European porcelain has attained. The fine Dresden porcelain, that of Berlin, the French porcelain, and the finer kinds which are formed in this country, are manufactured of such clay, which, from the use to which it is applied, has received the name of Porcelain Earth, and which appears, in general, to be derived from the decomposition of the feldspar of granite. It appears also, that natural earths, containing magnesia, are used with advantage in the manufacture. Giobert analysed an earth of this kind, which had long been employed for this purpose, and considered as a clay of great purity, and found, to his surprise, that it contained no argil, but consisted almost entirely of carbonate of magnesia and silex *. It is not improbable, that what have been regarded as pure natural clays, may frequently have contained this earth.

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* Nicholson's Journal, vol. xii. p. 277.

The proportion of the earths to each other must likewise be of importance; and from differences in this respect, arise in part the differences in the porcelain of different countries, as well as the necessity frequently of employing mixtures of natural clays. The argil communicates tenacity and ductility to the paste, so that it may be easily wrought: the silex gives hardness and infusibility; and, on the proper proportion of these, depends in a great measure the perfection of the compound. The proportion of silex in porcelain of a good quality is, according to Vauquelin, at least two-thirds of the composition; and of argil, from a fifth to a third. An intelligent manufacturer has informed me, that magnesia is of utility, by lessening the tendency which the composition of silex and argil alone has to contract in baking, and which is inconvenient in the manufacture. From what we know, however, of the fusibility of an artificial mixture of these earths, a large proportion of magnesia must render the composition too fusible.

In the manufacture of the finer kinds of porcelain, the ingredients are carefully washed, dried, and ground by a mill to a very fine powder, which is passed through a sieve. This is made into a paste with water, which is well kneaded, so as to be uniform in composition, or, to avoid the labour of this, is diffused in water, so as to form a liquid of the consistence of cream, from which the superfluous water is dissipated. The vessels shaped from this paste are baked in earthen pots, to render them tolerably hard and compact: they are then covered with the materials for glazing, which, in the better kinds of porcelain, consist of a mixture of earths, which form a compound more vitrifiable than the porcelain itself. These materials are diffused in a very fine powder in water, into which the baked vessels are dipt: the surface is thus covered with a thin crust, the water being absorbed. When dry, they are again placed in the earthen pots or seggars, and exposed to a very intense heat. The solid matter of the porcelain undergoes a semi-vitrification, whence it possesses all the hardness of glass, and has an additional value in being less brittle, and much more able to bear sudden alterations of temperature: it derives also much beauty from its semi-transparency and white colour. The glazing on the surface is, from its greater fusibility, more completely vitrified, and is, of course, more smooth and impervious.

With regard to the theory of the kind of vitrification which constitutes porcelain, the opinion advanced by Reaumur, who first investigated this subject, has been generally received. He supposed, that in porcelain, part of the matter has been completely vitrified by the heat, and is thus in the state of a glass; while another part has remained infusible, is diffused through this, and diminishes its transparency, or gives it its whiteness and semi-transparency. In the coarser kinds of porcelain, the heat which has been applied, he supposes to have been such as to have produced merely a semi-vitrification, whence the substance remains opaque, but may be completely vitrified by a stronger heat. This last opinion is probably the just one with regard to every variety of porcelain; and even if the vitrification, or, more correctly, the fusion were complete, it would not follow that the result must be a transparent glass.

Mr Wedgwood, in the course of his experiments with the pyrometer, ascertained the fusibility of the principal porcelains. Several kinds manufactured in England underwent perfect vitrification, at temperatures from 90° of his scale to 120°. One kind, manufactured at Bristol, shewed no appearance of vitrification at 135°. The common Chinese porcelain did not vitrify completely by any heat, but began to soften at 120°, and, at 156°, became so soft as to lose its shape. The real Nankeen porcelain did not soften in any heat that could be applied: its internal substance even remained of its granular texture and porous. The Dresden porcelain was more refractory than the common Chinese, but less so than the Nankeen.

The inferior kinds of porcelain, or pottery, are prepared by the same process as that which has been described; less pure, but more fusible materials being employed, and of course a less degree of heat being applied. The better kinds of English stoneware are composed of pipe-clay, and pounded flints. The yellow stoneware is made of the same materials, in other proportions. The first is glazed, by throwing sea-salt into the furnace in which it is baked, when the heat is strong; the salt is converted into vapour, and this being applied to the surface of the stoneware, vitrifies it, and forms an excellent glazing. The yellow stoneware is glazed, by dipping the baked ware in water, in which is suspended a mixture of pounded flint, glass, and oxide of lead. In the glazing of some kinds of stoneware, oxide of tin enters into the composition with the oxide of lead, and gives a whiter glaze. All the coarser kinds of pottery are glazed with oxide of lead; this promoting so much the fusion and vitrification, that the low heat at which they are baked is sufficient.

An interesting branch of the art of making porcelain, is that of applying and fixing colours on its surface, and likewise of gilding it. The colours are always obtained from metallic oxides, and they are applied by fluxes, or enamels, which are more fusible than the matter of the porcelain. On this subject, some information has been given by Clouet * and Brogniart †.

The flux which is generally employed to fix the colours with more facility and uniformity on the porcelain, is either a mixture of vitrified oxide of lead and silex, or borax, or sometimes a mixture of all these. The advantage of this flux is, that, by promoting the fusion of the metallic oxide, it causes it to adhere at a lower heat than that by which it might be decomposed, and the colour changed; and hence, a larger quantity of flux is added to those colours which are most liable to change: it also serves as a medium of union with the matter of the porcelain, and renders the surface more smooth.

The method of applying them is, either to mix the metallic oxide, or mixture of oxides, which is to give the colour, with the materials of the flux, the whole being reduced to an impalpable powder, which is made into a thick liquid, either with gum-water, or with a volatile oil, and applied, by a pencil, to the surface of the unglazed

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* Philosophical Magazine, vol. vii. p. 1.

† Nicholson's Journal, 8vo, vol. iii. p. 101.

porcelain; or, in other cases, the colouring matter and the matter of the flux are fused together, and the enamel thus formed, being reduced to a fine powder, is applied in a similar manner. The first mode is generally employed with those colours which are liable to be altered by heat.

The oxides of different metals give different colours. Carmine red is obtained from the purple precipitate of the solution of gold by muriate of tin: violet is obtained from the same substance, when a larger quantity of oxide of lead is contained in the flux. A rose-red is obtained from oxide of iron, highly oxidized by the action of nitric acid: yellow, from a mixture of white oxide of antimony with oxide of lead and silex: blue, from oxide of cobalt: green, from oxide of copper; and brown, from various proportions of the oxides of manganese, copper, and iron mixed. And by mixtures of different oxides, numerous shades of colour are procured. In gilding porcelain, the gold obtained in a state of mechanical division, or perhaps in a slightly oxidized state, by decomposing the nitro-muriate of gold by heat, is applied by the medium of borax and gum-water, and, after having been fixed by baking the porcelain, is burnished. Platina is applied in a similar manner.

That variety of earthen ware of which retorts and crucibles are formed, is formed from a clay in which argil and silex are contained, or at least with the addition only of oxide of iron, and which, therefore, is extremely refractory. The clay of which the Hessian crucibles are manufactured, consists, according to Vauquelin's analysis of it, of 69 of silex, 21.5 of argil, charcoal 1, and 8 of oxide of iron. Brick and tile are made from the coarsest clays, exposed to a less strong heat.

Argil fuses with some metallic oxides, forming glasses or enamels more or less perfect. It exerts no action on the metals or the simple inflammables.

CHAP. VI.

OF SILEX.

SILEX, or Siliceous Earth *, is the principal constituent part of a very great number of earths and stones, as Rock Crystal, Quartz, Agate, Sandstone, and many others. The sand of rivers, and of the sea-shore in every country, consists chiefly of it: this sand is formed by the attrition of the solid strata over which the waters flow: the other earths which compose these strata are all of them more soluble in water than the siliceous, or are softer and more easily suspended and diffused; and hence it is deposited in small particles, and forms the sand.

It exists nearly in a state of purity in rock crystal; in some specimens of which it forms 99 parts in 100; in

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* Dr Pearson changed the term silex into silica, on the principle of giving the names of the earths a similar termination. It is impossible, however, to adapt this to the names of all of them: the termination itself too is not very conformable to the idiom of the language, and hence, when it cannot be established so as to give a systematic uniformity, there is no propriety in partially adopting it. I have therefore preferred the old and less harsh appellation of Silex.

flint it is nearly equally pure, amounting to 97 or 98 parts. It is from flint that it is generally procured. The usual process is to calcine common flints in a crucible, in an open fire, so as to render them brittle and easily reduced to powder. One part of the pounded flint is mixed with three or four parts of sub-carbonate of potassa, and exposed, in a silver bason, to a heat gradually raised, until the mixture is fused, in which state it is to be kept for a short time. When cold it is to be dissolved in water, the siliceous earth of the flint being rendered soluble by its combination with the alkali. To the solution diluted sulphuric acid is to be added as long as any precipitation takes place: the precipitate is washed with water, until the water come off tasteless: it is then dried, and is the pure silex. If the fusion of the silex and alkali has been performed in a crucible, the silex is always mixed, according to Bergman, with argil, from the earth of the crucible.

Mr Davy, in attempting to decompose silex by galvanism, found, that it is very little affected, partly from its insolubility, and partly from its being nearly in a state of indifference with regard to the negative or positive pole, resting equally at either, when placed in the electrical circuit, diffused in water. By employing the methods which have been described under the history of argil, appearances of decomposition were however obtained. Thus when the silex was fused with six parts of potassa, and placed in fusion in the galvanic circuit, metallic matter was obtained, from which, when exposed to the air, or dropt into water, a minute quantity of silex was regenerated. And a similar result was obtained, by electrifying negatively potassium, amalgamated with one third of mercury, in contact with silex. No product was obtained, however, in any of these experiments, which could be considered as the pure base. Were it procured, the name Silicium would belong to it.

Silex, when pure, is under the form of a white powder, the specific gravity of which is about 2.6. It is perfectly insipid, and is harsh and gritty to the touch : when mixed with water, it does not form an adhesive paste.

This earth is extremely infusible. It not only does not melt in the focus of the most powerful burning mirror, but, according to the experiments of Lavoisier *, confirmed by those of Guyton †, it remains without fusion, at least when in the state of rock crystal, in the still more intense heat excited by a stream of oxygen gas directed on burning charcoal. Mr Hare found it however to melt completely in the flame of a stream of oxygen and hydrogen gases, forming when cold a kind of enamel ‡.

This earth is very sparingly soluble in water, and under common circumstances appears even altogether insoluble. Bergman in his researches on silex, observed, that when the silicated potassa, or the liquor prepared from the solution in water of the compound of silex and potassa, is decomposed by an acid, if the solution has previously been largely diluted with water, no precipitate appears on the addition of an acid in quantity sufficient to saturate the alkali, nor is it even rendered sensibly turbid,—a proof that this earth, when in a state of division, is to a certain extent

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* Mémoires de l'Acad. des Sciences, 1783, p. 566.

† Journal de l'Ecole Polytech. Cah. III. p 298.

‡ Philosophical Magazine, vol. xiv. p. 304.

soluble in water. It has since been discovered to exist frequently in mineral waters in a state of solution. In the water of the Geyser fountain in Iceland, it is present to the amount of 9 or 10 grains in 100 cubic inches of water: and although a small quantity of alkali is also present, amounting, according to Dr Black, to 1.5 grains, according to Klaproth, to 3 grains; this, from what we know of the power of the alkalis to hold silex in solution, is, independent of the solvent power of the water, in too small quantity to dissolve this quantity of silex; this alkali, too, is in the state of carbonate, by which its solvent power with regard to this earth is diminished. Silex also exists in solution in other mineral springs, as in the Bath waters, in which no alkali, nor any substance that can contribute to its solution can be detected *. Quartz stalactites also occur, with their surface covered with minute crystals,—a proof of the deposition of silex from a state of solution.

Silex is very sparingly soluble in acids, and is scarcely capable, in any case, of producing a neutral compound. By fusion, it combines with boracic and phosphoric acid, and forms a transparent glass; and, even in the humid way, when in that state of division in which it is when precipitated from its alkaline solution, it has been supposed to be dissolved in small quantity by these acids. Muriatic acid dissolves it still more sensibly: the solution is limpid, and has always an excess of acid. When concentrated by evaporation, it assumes, according to Fourcroy, a gelatinous consistence, and, if boiled, is decomposed; the silex, with perhaps a portion of the acid, being precipitated in a gra-

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* Nicholson's Journal, 4to, vol. iii. p. 103.

nulated powder *. The fluoric acid, however, is its proper solvent: it retains it in solution in the gaseous form, and likewise a portion of it when the acid is combined with water. From a solution of this kind, even crystals have been obtained, which have been considered as the compound of silex and fluoric acid. The consideration of this combination rather belongs, however, to the history of this acid.

The chemical relations between silex and the fixed alkalis are important. They form very perfect combinations, which differ in their properties, according to their proportions. With a large quantity of alkali, the compound is soluble in water: with a smaller quantity it is insoluble.

The combination can be effected even in the humid way. If on silex, in a state of extreme division, an alkaline solution be boiled, a quantity of the earth is dissolved, and the liquor, even though diluted pretty largely with water, forms a jelly on cooling.

If one part of any pure siliceous fossil, as quartz, or flint, reduced to powder, be exposed, with three parts of sub-carbonate of potassa, to a heat gradually raised to redness, they enter into fusion; the materials swell considerably, and an effervescence even takes place from the disengagement of water and carbonic acid: a species of glass or frit is formed, which is deliquescent on exposure to the air. When water is added to it, a solution is effected; part of the earthy matter, however, being in general left undissolved: the matter dissolved is the compound of the silex with the alkali, retaining still a little of its carbonic

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* System of Chemistry, vol. iii. p. 297.

acid. If pure potassa has been employed in the experiment, the fusion is more complete, the glass formed more perfect, and entirely soluble in water. When the solution of silicated potash, or soda, as these compounds have been named, is concentrated by evaporation, it assumes a gelatinous consistence. Even by large dilution with water, it is partially decomposed, as Bergman observed, and a portion of silex is precipitated ; the affinity of the alkali to it being weakened by the affinity and quantity of the water. It is decomposed by all the acids, even by the weakest, and the earth thrown down in the form of a spongy precipitate.

The silex, either pure, or in combination with a little alkali, appears, under certain circumstances, to be capable of crystallizing from this liquid. Trommsdorff having observed, that, in a bottle in which liquid silicated potash had stood for eight years, crystals were deposited, examined them, and found they were tetraedral pyramids, transparent, and so hard, that they gave sparks with steel: they were soluble in liquid potassa, and in fluoric acid *.

When a smaller proportion of alkali is employed in this combination, the compound is less soluble in water, and a stronger heat is required for its vitrification ; and when the proportion of alkali is not more than half that of the earth, it is possessed of considerable hardness, and great transparency, is permanent in the air, and insoluble in water. This is the well-known compound GLASS, one of the most beautiful and useful products of art. The following is an outline of the process by which it is formed :

Two parts, by weight, of siliceous earth, are mixed with

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* Annales de Chimie, tom. xxii. p. 118.

from one part to one and a half of the carbonate of potash, or of soda, of commerce. These are the essential ingredients of glass: they are intimately mixed, and the mixture is exposed to a strong heat in a furnace, to expel the water and carbonic acid, and to effect an imperfect combination between the alkali and earth. When this operation is completed, it forms what is named the Frit. Large pots made of clay, and placed in a furnace, are filled with this frit: heat is applied sufficient to fuse it, and the melted mass is kept in fusion for some time, till the whole appears to be uniform. This forms the glass, which is then ready to be worked. The unvitrified matter which rises to the surface is withdrawn.

The transparency, and other estimable qualities of the glass, are greater, as the materials have been pure. The finer kinds of glass, crystal glass, as it is named, is from the best pearl-ash with pounded flints, or a very white sand washed. Window glass is from sand and kelp. Green bottle glass is from sea-sand, and the refuse of the soapmakers' ley, which contains more lime than alkali. The proportions of the ingredients have likewise a material influence on the qualities of the glass. The less alkali is present, the more heat is requisite for the vitrification; but the glass is also more hard, and less liable to be altered by exposure to air or moisture.

Though the alkali and siliceous earth produce a perfect glass, yet, in the manufacture of it, various additions are made for different purposes. The most essential addition is oxide of lead, either litharge or minium. It promotes very much the vitrification of the materials; and what is of more importance, it renders the glass more dense and ductile, and consequently susceptible of a higher polish, and adds much to its refractive power, and of course to its lustre. Hence it always enters largely into the composition of ornamental glass, and of flint glass or crystal. It renders the glass at the same time softer, and hence it is more liable to be scratched; it gives also more fusibility.

Another metallic oxide used in the preparation of the finer kinds of glass, is the black oxide of manganese. The intention with which it is added is to improve the whiteness and transparency, effects which it produces by imparting oxygen. This serves in part to consume the inflammable matter that may be mixed with the materials, but its operation is principally on the oxide of iron, which is always more or less present. The theory of its action was very well explained from the researches of Scheele, by Bergman. Iron, in a low state of oxidizement, gives to glass a green tinge, while, if it be at a high degree of oxidizement, it either does not enter into fusion with the ingredients of the glass, or at least it does not communicate any colour. Manganese, on the contrary, in the state of black oxide, gives a violet colour, while, when reduced to the white oxide, the glass is colourless. In adding, therefore, the black oxide to glass, while it yields its oxygen to the iron which it thus brings to a high state of oxidizement, it itself passes to the state of white oxide, and thus each metal is in that state in which it does not communicate colour. To attain this, however, it is obvious that a certain proportion must be observed; for if there be an excess of the black oxide of manganese, it will produce a purple tint, while, if there be a deficiency of it, the green from the iron will prevail; and, accordingly, from the difficulty of fixing the precise proportion, glass has very generally a slight shade of one or other of these colours. Nitre is sometimes used for the same purposes as the oxide of manganese. Borax enters into the composition of the glass used to imitate the gems. Oxide of arsenic is used as a flux, and to correct the purple tint from manganese.

When glass is in fusion, it has a great degree of tenacity and ductility; at the same time, it has the property of adhering to a metallic tube or rod. Hence, small quantities of it can be easily removed from the furnace, can be blown into any shape, be cast into molds, and cut and wrought in a variety of forms.

Though glass at a high temperature has so much ductility, at a low temperature it is extremely brittle. If it is hastily cooled, this brittleness is so great, that the slightest agitation, even that excited by the solar rays, or by the undulations of the atmosphere, is sufficient to break it into minute fragments. This is remedied by the process of annealing. The glass, after it has been blown or cast into vessels, is removed into a furnace, the heat of which is not sufficiently high to melt or soften it; and the vessels are gradually removed from the hottest part of this furnace to the part where the temperature is lower, and are thus very slowly cooled. The brittleness of the glass hastily cooled, seems to be owing to the regular arrangement of the particles, or the disposition they have to remain in certain positions being disturbed; and the utility of the gradual reduction of temperature consists in allowing this arrangement to take place.

Glass, properly prepared, is scarcely acted on by any chemical agent. With the exception of fluoric acid, the most powerful and concentrated acids may be kept in it without suffering any change. From the experiments on the repeated distillation of water from glass-retorts, already stated under the history of that fluid, it appears, however, to be slowly eroded and decomposed at a high temperature, probably from the affinity exerted by the water to the alkali. When fused with an alkali, it is rendered soluble in water. And, as has been already stated, the newly discovered agents, potassium and sodium, decompose it from their strong attraction to oxygen, in consequence of which they partially abstract the oxygen from its alkaline, and perhaps also from its earthy, matter.

A change extremely singular, to which glass may be subjected, is what has been named its Devitrification. In the manufacture of glass, it often happens that masses of it lose the glassy character, become opaque, and exhibit an appearance of crystallization in their structure, rays diverging from different centres; and it had been observed that glass assumed these properties when it had been slowly cooled from a state of fusion. This was investigated by Sir James Hall, who proved that the slow cooling was the sole cause of this change; a piece of green glass being made to assume the stony character, by slow cooling, after fusion, and being restored to the state of glass, when again fused and cooled hastily, and this repeatedly, even on the same specimen. He extended his experiments to various natural substances, varieties of basalt and grunstein, which, by fusion, afford glasses, and established the same fact with regard to them; and one still more singular, that the substance, when it has the stony character, is much less fusible than when it has the vitreous, softening in the one state at from 15 to 24 of Wedgwood, in the other at from 32 to 38 *. The want of transparency and the crystalline structure may be easily supposed to arise from the arrangement into which the particles of the fused substance are allowed to pass by slow cooling; but there is some difficulty in assigning an adequate cause for the fusibility of the substance being different in the one state from what it is in the other, at least if no separation of the principles of the glass, but merely a change in the state of aggregation take place.

The change which glass suffers when it is exposed to heat, imbedded in gypsum, or in other earthy substances, by which it loses its transparency, acquires more hardness, becomes less fusible, and more capable of bearing sudden alterations of temperature, is probably of a similar kind. Glass thus changed, has received the name of Reaumur's Porcelain; this chemist having first observed its production and properties.

A branch of the art of glass-making is that of imitating the gems, or the making those coloured glasses named Pastes. The basis of these compositions is a pure glass prepared from pounded quartz, fused with an alkali, with the addition of borax, and of oxide of lead. The latter gives density to the glass, a susceptibility of receiving a higher polish, and a greater refractive power, by which, of course, the lustre is increased. Different colours are obtained from the addition of various metallic oxides. Gold gives a red, cobalt blue, manganese purple, lead

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* Edinburgh Philosophical Transactions, vol. v.

yellow, iron green; and these colours are so rich, as to be equal, or even often superior to those of the natural gems; though in lustre, hardness, and consequently in durability, the pastes are always far inferior. They are easily distinguished by their inferior specific gravity, and their softness, which is such that they can be scratched by the knife. Very complicated recipes were formerly given for their preparation, which are collected in the works of Kunckel and Neri, and which have been gradually simplified. A series of experiments on the subject, in which processes for imitations of the different gems are given, is inserted in the Journal de Physique, tom. xxviii. p. 502.

When glass is fused with a large quantity of oxides of tin and lead, it becomes white and opaque. This forms what is named Enamel.

Silex exerts affinities to the other earths. It unites with barytes by fusion, and their mutual attraction is also exerted in the humid way. If one part of silex be mixed with three parts of barytes, and be exposed to heat in a platina crucible, a compound is formed, which has not the acrid taste of barytes, nor does it slake with water, but is soluble in all the acids, even the weak acetic, the barytes communicating this solubility to the silex. Silex, too, is precipitated from its alkaline solution by barytes, the two earths entering into combination. Strontites exerts a similar action on silex. Vauquelin found, that when the former earth is mixed with one-third of its weight of the latter, and exposed to a strong heat, a mass is formed, not capable of slaking in water; but when pulverized and boiled in water, a portion of it is dissolved, and from this solution silex is precipitated by nitric acid. The strong attraction between lime and silex is displayed, in lime-water producing a precipitate, when added to silicated potash; this precipitate being a compound of the two earths, the affinity of the lime to the silex having therefore overcome the affinity of the potash to that earth. These two earths unite also by fusion. When in equal parts, they melt, according to Mr Kirwan's experiments, at a heat not exceeding 150° of Wedgwood, and form a white enamel, semi-transparent, and so hard as to strike fire with steel. When the proportion of lime is only one-fourth that of the silex, the compound is not fused at 156°. It has been supposed, that on the affinity which these two earths can mutually exert, even in the humid way, depends, in part at least, the induration of mortar. This is, no doubt, principally to be ascribed to the intimate union of the lime with the water of the mortar, and perhaps to the gradual absorption of carbonic acid from the atmosphere; but the advantage derived from the intermixture of sand, though it is in part of a mechanical nature, is probably also partly owing to the affinity exerted between the siliceous particles and those of the lime. Between magnesia and silex the mutual attraction is weak. When mixed in equal weights, they do not unite but at a very intense heat,—that excited by oxygen gas directed on burning charcoal, when they fuse into a white enamel so hard as to scratch glass *. The relation of silex to argil has been described under the preceding chapter.

Silex vitrifies with some of the neutral salts, particular-

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* Mémoires de l'Acad. des Sciences, 1783, p. 600.

ly with borax, and with the alkaline phosphates. It also combines by fusion with a number of the metallic oxides. It does not exert any action on the metals, or on the inflammables.

CHAP. VII.

OF ZIRCON.

THIS earth was discovered by Klaproth in the Zircon or Jargon, a gem brought from Ceylon. It was afterwards found also in the hyacinth. It is extracted from the zircon, by reducing it to fine powder by repeated calcination, and fusing it with five or six times its weight of pure potassa, keeping the mixture in fusion for two hours: the mass is then lixiviated with water, to extract the superfluous alkali. It is dissolved in dilute muriatic acid: this solution is boiled, to cause the deposition of the silex: the liquid is filtered, and carbonate of soda added, by which the zircon is precipitated in the state of carbonate: from this the carbonic acid is expelled by heat, and the pure earth is obtained.

Mr Davy having submitted zircon to the action of galvanism, in the manner already described under the history of argil and of silex, obtained results indicating decomposition; the product, when the zircon had been electrified in contact with soda, or with potassium, decomposing water, and affording a white powder which had all the characters of zircon. There is every probability, therefore, that zircon is analogous in constitution to the other earths.

Zircon, obtained by the process above described, is in a white powder, insipid, and somewhat rough. When exposed, imbedded in charcoal, to the violent heat of a forge, it undergoes a semi-vitrification: it becomes so hard as to give fire with steel; has a brilliant vitreous fracture; and is of a grey colour. In this state, its specific gravity is 4.3.

When zircon in powder is mixed with water, it imbibes it, and forms a semi-transparent jelly, and it retains so much of this in drying, as to form a substance in appearance like gum. It exerts, therefore, some affinity to water, but it is not entirely dissolved by it.

It combines with the acids, and forms salts in general sparingly soluble. Those which are soluble have a sweetish astringent taste. These compounds are not easily formed by direct combination, unless the earth is in a loose state, as when it is newly precipitated; and its affinities to the acids appear weak, as its salts are in general decomposed by a low heat, as well as by the alkalis, and all the other earths.

Zircon is insoluble in the liquid alkalis, but is dissolved by the alkaline carbonates; hence, in preparing it, care must be taken not to add an excess of carbonate of soda. Its relations to the earths are scarcely known. It may be fused with silex and with argil, and a mixture of these three earths is more fusible than a mixture of two of them. It appears to combine too by fusion with some of the metallic oxides. On the inflammables it exerts no action.

CHAP. VIII.

OF GLUCINE.

THIS earth was discovered by Vauquelin, forming a constituent part of the beryl and of the emerald, and to him we are principally indebted for a knowledge of its properties *. His experiments have been confirmed by Klaproth †. Its name of Glucine is derived from the property it has of forming salts having a sweet taste.

The process by which Vauquelin obtained Glucine from the beryl, was to fuse one part of it with three parts of potassa; the mass, after cooling, was diffused in water, and dissolved in muriatic acid: the solution is then evaporated to dryness, and, on again dissolving it in water, the silex present remains undissolved. The solution is decomposed by sub-carbonate of potassa: the precipitate is digested with a solution of pure potassa; the greater part of it, consisting of argil, with a portion of glucine, is dissolved; but there remains a portion undissolved, which is the glucine, coloured by a small portion of oxide of iron.

Mr Davy, in attempting the decomposition of Glucine, obtained results similar to those from zircon, an amalgam being formed, when it had been placed in the galvanic

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* Nicholson's Journal, 4to, vol. ii. p. 358. 395.

† Analytical Essays, vol. ii. p. 176.

circuit with mercury and potassium which decomposed water, and which reproduced glucine, when the alkali in the liquid was neutralized by an acid.

Glucine when obtained pure is perfectly white, soft to the touch, and adheres a little to the tongue: it is insipid: is infusible: insoluble in water, but forms with it a paste which is somewhat ductile; this paste is not hardened by heat, nor does it contract. Its specific gravity is 2.96.

Glucine combines readily with the acids; its salts are generally soluble, and have a sweet taste.

They are decomposed by the alkalis: the earth is even completely precipitated by ammonia, which distinguishes it from argil. It is soluble in the fixed alkalis, but not in ammonia; it is dissolved, however, in carbonate of ammonia, forming a triple salt,—a property characteristic of it, though possessed also by zircon. It decomposes the salts of argil; which proves its difference from that earth, to which, in many of its properties, it has considerable resemblance. Its relations to the other earths are not known. With borax it melts into a glass.

CHAP. IX.

OF ITTRIA.

THIS earth was discovered by Gadolin, a Swedish chemist, in a fossil found at Ytterby in Sweden, which has since received the name of Gadolinite, and in which it is combined with silex and lime. The discovery was confirmed by Ekeberg, Klaproth, and Vauquelin; and the same earth has been discovered in some other fossils, particularly combined with the newly discovered metal, tantalium. In several of its properties ittria resembles glucine, particularly in forming salts of a sweet taste, and in being soluble in carbonate of ammonia; but it differs entirely in others.

The process followed by Vauquelin to obtain the earth from the gadolinite, was to dissolve it with the assistance of heat in diluted nitric acid, pouring off the solution from the undissolved silex. The liquor is then evaporated to dryness, by which any remaining silex, and any oxide of iron, is separated from combination with the acid. By redissolving the residuum in water, the compound of nitric acid and ittria is obtained: if there are any traces of iron, the liquor is either again evaporated to dryness, or a little ammonia is added; and after the separation of the oxide of iron in yellow flakes, the solution is decomposed by ammonia, which precipitates the new earth *. The process employed by Klaproth is similar; nitro-muriatic acid being employed; the iron being removed by the action of succinate of soda; and the ittria being precipitated by carbonate of soda †.

Ittria is obtained in the form of a white powder, insipid; it is heavier than any other earth, its specific gravity, according to Ekeberg, being 4.842. It is not fusible alone, but with borax it forms a white glass. It is not soluble in water, but it retains that fluid with considerable force.

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* Philosophical Magazine, vol. viii. p. 369.

† Analytical Essays, vol. ii. p. 47.

Ittria combines with the acids; its salts, as has been remarked, having generally a sweetish taste. Several of them too are coloured,—a property in which it differs from all the other earths. These salts are decomposed by the three alkalis, and by lime, strontites, and barytes.

Ittria is not dissolved by the liquid alkalis; nor do they redissolve it when added in excess, after having precipitated it from its solutions. This affords a distinguishing character between it and glucine. It is soluble in carbonate of ammonia, a property in which it resembles glucine, but it requires five or six times more of the carbonate for its solution than glucine does.

Prussiate of potassa throws down from its solutions a granular precipitate, of a white or pearl-grey colour. It is also precipitated in grey flocculi, by the watery or spirituous infusion of galls; but very slightly by the pure gallic acid. It is not affected by sulphuretted hydrogen, or hydro-sulphuret of ammonia, added to its solutions.

The great specific gravity of this earth, its forming coloured salts, and being precipitated by the alkaline prussiates and by tannin from its solutions, in some measure connect it with the metals, and lead to the suspicion that it is a metallic oxide. It is not reduced, however, to the metallic state by heating it with charcoal, but it runs with it into a kind of semi-fluid mass, which is heavier than the earth itself. Mr Davy has not submitted it to the action of galvanism.

BOOK V.

OF ACIDS AND THEIR BASES.

UNDER the view of the chemical relations of bodies, prefixed to this volume, and also under the consideration of the general chemical agency of oxygen, it has been stated, that the compounds of this element form two very extensive orders,—Oxides and Acids. The former have scarcely any common characters by which they can be distinguished, farther than their chemical constitution; the latter are characterized by certain properties which belong to all the individual acids. These characters, and the general chemical relations of these substances, I have now to point out, before proceeding to their individual history. As a natural order, they are well distinguished from all others; and as chemical agents, they are of the first importance, from the numerous and energetic affinities they exert.

Acids are all sour to the taste; and this property of sourness, as it is named, exclusively belongs to them, or rather every body which tastes sour is ranked as an acid; some retain this sourness when diluted with a very large quantity of water, even with more than 1000 times their weight; others require to be tasted in their concentrated taste, to excite this sensation. They are more or less caustic considered with respect to their action on animal matter, though this quality is likewise possessed by the different acids in very different degrees. They change to a red, the blue, purple and green colours of vegetables; and this is in general their most obvious and delicate test. The greater number of them have an attraction to water; some of them cannot be obtained free from it, but being combined with it, exist in the fluid form; others, which are capable of being rendered solid, or which pass into the state of gas, still absorb water with avidity when it is presented to them. There are a few acids, however, which are very sparingly soluble in water.

The acids combine with the alkalis, and form compounds, in which both acid and alkaline properties are lost. These two classes of substances may be regarded as opposed to each other, or as possessing distinguishing properties, incompatible, which tend to destroy each other, and which cannot exist at the same time in the same combination, both being lost when they are united in certain proportions, or the properties of either appearing according as it is predominant in the combination. If to any acid, a portion of an alkali be added, the acidity is diminished in proportion to the quantity of alkali added; this diminution will proceed according as the alkali is added, until at a certain proportion none of the characteristic properties of the acid appear in the combination; the sour taste is entirely gone; it does not redden the most delicate vegetable colours; nor is it possessed of any causticity. At the same time, neither do the properties of the alkali appear, but by continuing to add it, so as to render it predominant in the combination, they become apparent, and thus numerous shades of combination may be established. When the acid and the alkali are combined in that proportion in which the characteristic properties of both are lost, they are said to be mutually saturated or neutralized, and the compound they form in this state is named a Neutral Salt.

At the stage of neutralization it generally happens, that from the condensation which attends the combination, there is a greater tendency to cohesion than at any other, and hence the neutral compound assumes the solid state, unless a large portion of water be present to keep it dissolved. So far even does this tendency to cohesion in this state prevail, that the separation of the neutral compound takes place sometimes from a liquor in which there is an excess of acid or of alkali. It does not always happen, however, that the tendency to cohesion is exerted with greatest force at the precise point of neutralization; in some cases the compound separates with an excess of acid, or of alkali.

In these latter cases it was supposed, that the substance thus produced is a compound of the neutral salt, with an excess of one of its ingredients; and even in all cases it has been imagined, that an acid and alkali have a tendency to combine in that proportion which constitutes neutralization, and that other compounds of them are to be regarded as combinations of this neutral compound, with an excess either of acid or of alkali. There is no reason, however, to infer, that such combinations are of this indirect kind. The simple view consistent with all the phenomena, is, that an acid and an alkali are disposed to unite in every proportion,—that each weakens the properties of the other, in proportion to the quantity of it in the combination,—that therefore there is one proportion in which these opposing properties must be mutually saturated or neutralized; and that the force of cohesion determines the separation of the compound from the fluid in which it is formed, and thus apparently gives rise to a fixed or determinate proportion being observed. But when this does not happen, there is no interruption of the progress of the combination, and it therefore takes place in every proportion. This separation will always take place where the tendency to cohesion is greatest; it coincides sometimes with the point of neutralization; sometimes not. That it should be at the point of neutralization, seems to follow, from this being the point at which the elements of the compound exert their respective energies with greatest power; it may deviate from it, however, where one of the elements has a greater tendency to solidity than the other, the compound separating with an excess of that ingredient. This is the view at least which has been given by Berthollet *, though, as has already been observed, there are some facts which do not altogether accord with it.

To effect this neutralization of properties, very different quantities of the different acids are necessary in relation to the alkalis, and the same holds true in the neutralization of the alkalis by the acids. Berthollet supposes, that the energy of the respective affinities of the acids, is indicated by this power of saturating or neutralizing the opposing alkaline properties, as that of the affinities of the alkalis may be judged of from their power of neutralizing

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* Chemical Statics, vol. i. p. 36. 257.

the acids; the less of any substance which is requisite to saturate a given quantity of another, the stronger being its attraction toward it *. The old opinion, on the other hand, was, that the affinities of the substances were to be judged of by their power of dislodging each other from combinations in which they exist,—an opinion which can scarcely be maintained, as these decompositions arise not merely from the relative forces of affinity, but from other circumstances by which attraction is modified. On this subject some observations have been already made, at sufficient length.

The action of the acids on the earths is perfectly similar to that on the alkalis; they produce, by their combination, a mutual neutralization of properties, and compounds are formed which belong to the order of neutral salts. They also neutralize very different quantities of the acids, and in this respect differ widely from each other; and one earth, silex, seems scarcely capable of producing the state of neutralization. The tables of Kirwan and Richter, comprizing the results of their investigations on this subject, have been already given. (Note A g.)

The action of the acids upon the metals is somewhat more complicated. The metal never combines with the acid directly, but if it is first combined with oxygen, so as to form an oxide, it unites with it readily. Hence if a metallic oxide is added to an acid, for which it has an attraction, a direct combination is formed, and a compound termed a Metallic neutral salt produced. If the metal is added to the acid, it is frequently able to decompose it,

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* Chemical Statics, vol. i. p. 45.

and attract part of its oxygen, or to decompose the water it contains, and receive from it oxygen; and in either of these cases the metallic oxide thus formed, unites with the remaining acid, and a salt is formed. But if the metal is unable to effect either of these decompositions, either that of the acid or of the water, no combination whatsoever takes place, but it remains unchanged. The theory of these relations between metals and acids has been already given. (Note A d.)

The various compounds formed by the combination of the acids with the alkalis, earths, and metallic oxides, and named Neutral Salts, have certain properties by which, as an order, they are characterized, which it is necessary to state, as well as some observations on their general properties; as the history of these salts, at least those with alkaline and earthy bases, is to be given under the history of the individual acids by which they are formed.

In general the neutral salts are soluble in water, but they differ much in the degree of solubility. Some have so strong an attraction for that fluid, that they require to be exposed to a strong heat to obtain them solid; some dissolve in half their weight of water, some require an equal weight, double, or more, others take 500, 1000, or 2000 times their weight. Chemists have agreed to term those salts Insoluble, which require for their solution more than 1000 times their weight of water. The solution of salts in water is accompanied with a change of temperature, generally a diminution, and that in some cases to a considerable extent. This is owing to the enlargement of capacity attending the solution, from the transition of the solid salt to the fluid form.

The solution of salts is generally promoted by an increase of temperature. In different salts the increased solubility from this cause is very different; the quantity dissolved by a certain increase of temperature in a given quantity of water, being in some doubled, in others tripled, while there are some salts, sea-salt for example, which dissolve as abundantly in cold as in boiling water. This difference depends on their relative forces of cohesion; those which have their cohesion most weakened by a given temperature, in other words, which are fusible with the least increase of temperature, having their solubility in water most augmented by the addition of caloric.

When a salt has been dissolved in water, it may be recovered by evaporation of the water, and it will appear in a regular or irregular figure, according as the evaporation has been conducted. If it has been rapid and carried to a considerable length, a powder falls to the bottom, which augments as the liquor cools. If, on the contrary, the solution has been boiled down to a certain point only, and cooled, the salt concretes slowly, and in those regular transparent masses, termed Crystals. This susceptibility of crystallization is stated as a distinguishing property of salts, since the greater part, perhaps all of them possess it, and since it is more remarkable in them than in other bodies. In different salts the figure of the crystals is very different, and such a difference obtains even in the same salt, according to the quantity of it contained in the solution when the crystallization commenced. But by attention to the quantity, temperature, and other circumstances, the same salt may be always made to assume the same figure. In some cases regular crystals cannot be obtained, when the solution of a salt is hastily evaporated and set to cool; but by slow and spontaneous evaporation, crystals are obtained even more regular in their figure, and denser in their texture than those that are hastily formed.

When salts are crystallized, they always retain a quantity of water which is essential to the constitution of the crystal. Some retain even half their weight of water, others only a very minute portion The water of the crystal exists in it in the solid form, as is evident from the great quantity of it contained in the salt, and it is accordingly found, that the solution of a crystallized salt in water, is attended with a greater diminution of temperature than the solution of the same salt in an uncrystallized state, as in the former case the water absorbs caloric in passing to the fluid form.

Several characters which serve to distinguish the salts when they are crystallized, depend on this water of crystallization. Thus some, when exposed to a moderate heat, melt, but if the heat be continued, a white crust appears on the surface, and this increases till the whole is converted into a dry mass, to fuse which requires a heat much more intense. This is termed the Watery Fusion of Salts. It takes place in those which contain a large quantity of water of crystallization, and which are more soluble in hot than in cold water. The application of the caloric enables the water to dissolve the salt, but as this water is soon evaporated by the continued heat, the solid salt is left, and may be made to undergo a real fusion, by giving it the necessary increase of temperature. Other salts when exposed to heat are quickly split, with a crackling noise. This is termed Decrepitation; it takes place in those salts which have little water of crystallization, the increased temperature converting that small quantity into vapour, by which the crystals are suddenly burst. Some salts when in crystals lose their transparency by exposure to the air, are covered with a white crust, and at last fall entirely into powder. This is termed Efflorescence ; it depends on the abstraction of their water of crystallization by the attraction exerted to it by the atmospheric air. There are others, on the contrary, that have so strong an attraction to water, that they absorb it from the atmosphere, and consequently soon become fluid. This property is termed Deliquescence, and such salts are named Deliquescent.

By these different properties, as possessed by different salts, we are often able to distinguish them from each other, without examining their chemical composition. The figure of the crystals is particularly important for this purpose, though the other properties likewise make always part of their distinctive descriptions.

A very important problem in chemistry is, that of determining the composition of neutral salts, not merely as to their ingredients, but as to the proportions in which these are combined ; a knowledge of this being frequently of great importance in chemical analysis. The subject has accordingly engaged the attention of several eminent chemists. Bergman began the investigation, and from a series of experiments gave tables of the proportions of the ingredients of a number of salts. Wenzel prosecuted the subject : but Mr Kirwan is the chemist who has bestowed the greatest labour on it, and whose experiments may be regarded as affording the most accurate results. The investigation is indeed attended with peculiar difficulties.

It might be supposed at the first glance, that nothing is easier than to determine what quantity of an acid combines with an alkali or earth, so as to form a neutral combination, and that, therefore, from such an experiment the composition of such a compound, both with regard to its principles and their proportions, might be determined; and could we indeed obtain the ingredients pure and insulated the experiment would be easy. But the difficulty arises from the impracticability of procuring them in such a state; the acids, in particular, cannot be obtained free from water; they do not even part with it entirely when they enter into these combinations, and form compounds perfectly solid and dry; and hence the whole investigation, if it is to be rendered accurate, must be founded on the preliminary one of the quantity of real acids, in acids of given strength, as estimated either by specific gravity, or by any other test. It was chiefly from not attending to this point, that the experiments of Bergman and Wenzel are comparatively of less utility, and it is on this investigation that Mr Kirwan has bestowed so much care. His researches were published in the Philosophical Transactions for 1781 and the two succeeding years: but being sensible that the principles on which he had founded his calculations were not correct, he resumed the investigation some years afterward, and published the results in the 4th and 7th volumes of the Transactions of the Irish Academy. The method being complex, involving considerable detail, and the discussion with regard to the certainty of the results being rather difficult, and not elementary, I shall refer the statement of this subject to a note, and give here the results with regard to the principal salts, in a table which Mr Kirwan has drawn up. Note F.

Table of the Composition of Salts,

SALTS.	BASE.	ACID.	WATER.	STATE.
Carbonate of potassa	41.	43.	16.	Crystallized
Pearl-ash - -	60.	30.	6.	Dry
Carbonate of soda -	21.58	14.42	64.	Fully crystallized
ditto -	59.86	40.05	-	Desiccated
barytes	78.	22.	-	Natural or ignited
strontites	69.5	30.	-	Natural or ignited
lime -	55.	45.	-	Natural if pure *
magnesia	25.	50.	25.	Crystallized
common do.	45.	34.	21.	Dried at 80°
Sulphate of potassa -	54.8	45.2	-	Dry
soda -	18.48	23.52	58.	Fully crystallized
ditto -	44.	56.	-	Desiccated at 700°
ammonia	14.24	54.66	31.1	
barytes -	66.66	33.33	-	Natural and pure *
strontites	58.	42.	-	Natural and pure *
lime -	32.	46.	22.	Dried at 66°
ditto -	35.23	50.39	14.38	Dried at 170°
ditto -	38.81	55.84	5.35	Ignited
ditto -	41.	59.	-	Incandescent
magnesia -	17.	29.35	53.6	Fully crystallized
ditto -	36.68	63.32	-	Desiccated
Alum - -	12. †	17.66	51. ‡	Crystallized
Ditto - -	63.76	36.25	-	Desiccated at 700°
Nitrate of potassa -	51.8	44.	4.2 §	Dried at 70°
soda -	40.58	53.21	6.21 §	Dried at 400°
ditto -	42.34	57.55	-	Ignited
ammonia	23.	57.	20.	
barytes -	57.	32.	11.	Crystallized
strontites	36.21	31.07	32.72	Crystallized
lime -	32.	57.44	10.56	Well dried in the air
magnesia -	22.	46.	22.	Crystallized
Muriate of potassa -	64.	36.	-	Dried at 80°
soda -	53.	47. ‖	-	Dried at 80°
ammonia			-	Crystallized
ditto -	25.	42.75	32.25	Sublimed
barytes -	64.	20.	16.	Crystallized
ditto -	76.2	23.8	-	Desiccated
strontites	40.	18.	42.	Crystallized
ditto -	69.	31.	-	Desiccated
lime -	50.	42.	8.	Red hot
magnesia	31.07	34.59	34.34	Sensibly dry

* Or artificial ignited. † Ignited.

‡ Of Crystallization + 19.24 in the base.

§ Of composition. ‖ Aqueous, 38.88 real.

It remains only to explain the nomenclature of the acids, and of the compound salts which they form. This is systematic and precise; and the substitution of this systematic nomenclature, instead of the arbitrary and unconnected one formerly in use, is one of the greatest benefits that has been conferred on the science.

All acids being compounds of oxygen with certain bases, the name of each is derived from the base of which it is formed. But as this base is often capable of combining with two proportions of oxygen, and of forming two acids different from each other, these must be distinguished, and this is done by a variation in the termination of the name, the syllable *ic* being the final one, when the acid is the one which contains the larger proportion of oxygen, and *ous* where it contains the smaller proportion. Thus sulphur, by combination with oxygen in two proportions, forms two acids; the word Sulphur is the radicle whence their names are derived; the one, that with the less dose of oxygen, is the Sulphurous Acid; the other, the Sulphuric. We have thus also the Phosphorous and the Phosphoric, Nitrous and Nitric, &c.

One or two acids combine with a still larger proportion of oxygen; which, however, rather impairs than augments their acid powers. To the names of these the word Oxygenated or Oxygenized, or the syllable *oxy*, as an abbreviation, is prefixed; as the Oxy-muriatic Acid. Mr Chenevix objects to the latter mode, as the syllable *oxy*, from its derivation, implies acid; and therefore oxy-muriatic acid must mean acid muriatic acid. The advantage of conciseness, and of a single name, however, is not to be neglected, and without attending to the remote derivation, the syllable *oxy* may, without impropriety, be used as an abbreviation of oxygen; such a practice being sufficiently common in our language.

Where the base gives rise to only one acid, the name terminates in *ic*, as in the example Carbonic Acid. The acids belonging to the vegetable and animal kingdoms have a compound base, from which the name cannot be derived; it is taken, therefore, generally from the substance from which they are principally formed or prepared, as the Citric, Malic, &c.

The nomenclature of the salts, formed by the union of the acids with the alkalis, earths, and metallic oxides, is equally systematic. All the salts which are formed from one acid, are considered as forming a genus, under which are placed as species the individual salts, formed by the union of that acid with these different bases. The generic name is derived, therefore, from the name of the acid; the specific name from that of the base. When the name of the acid of which the salt is composed, is that which terminates in *ic*, the final syllable of the name of the salt is *at*, or rather, as Mr Chenevix has remarked, *ate*; when, again, the name of the acid terminates in *ous*, that of the salt formed from it has the last syllable *ite*. Thus, all the salts formed from sulphuric acid, constitute a genus to which the same Sulphate is applied, and the species are designated by the addition of the name of the base, as the Sulphate of Soda, Sulphate of Potassa, Sulphate of Lime, Sulphate of Iron. Those, again, formed by the sulphurous acid, are named Sulphites, as the Sulphite of Ammonia, &c. On the same principle, we have Nitrates and Nitrites, Phosphates and Phosphites, Muriates, Carbonates, &c. When the acid is in that state in which the term Oxygenized, or the syllable *oxy* is prefixed to its name, the same term or syllable is prefixed to the name of the salt; as the Oxygenized Muriate or Oxymuriate of Potassa.

Salts, it has been remarked, are sometimes formed with an excess of acid or of base; and to denote these a peculiar nomenclature ought to be appropriated. By the French chemists, the phrases with an excess of acid, or an excess of alkali, were added to the usual names. The method proposed by Dr Pearson is more concise and elegant. The genus being formed from the acid, when there is an excess of acid in a salt, the epithet *super* is prefixed to the name: when a deficiency of acid, the epithet *sub*. We thus speak of the Super-sulphate of Potassa, the Sub-carbonate of Potassa, &c.

Where an acid is united with two bases, as is sometimes the case, the names of both bases enter into its name,—as the sulphate of Argil and Potassa, or the Tartrate of Potassa and Soda.

Though this nomenclature at first met with much opposition, it is now nearly universally adopted; and it is impossible to deny its merits. By the mere name of any salt, its nature is pointed out, the memory is aided, and a facility of nomenclature afforded in naming so extensive a series of compounds.

CHAP. I.

OF NITRIC ACID, AND THE COMBINATIONS OF ITS BASE WITH OXYGEN.

THIS acid is one of those which has been longest known to chemists. The salt named Nitre consists of it combined with potassa; and the method of procuring the acid from this salt, so as to obtain it at least in a diluted state, forming what has been named Aquafortis, was known even to the alchemists. The base of the acid is Nitrogen; and this principle having been already considered as a constituent of atmospheric air, we have only to deliver under this chapter the history of the acid, and of the other compounds which are formed by the union of its elements, oxygen and nitrogen, in different proportions.

Nitric Acid, according to its most accurate analysis, consists of 29.5 of nitrogen, and 70.5 of oxygen. These elements further combine in the proportion of 44 of nitrogen, with 56 of oxygen, forming a compound which exists in the gaseous form, and which has no acid powers, —the nitrous gas of chemists, or, according to the more appropriate, though perhaps not perfectly correct application which has been given to it, Nitric Oxide. From 63 of nitrogen united with 37 of oxygen, still another elastic compound is formed, likewise destitute of acidity, Ni-

TROUS OXIDE. And, lastly, nitric acid, when combined with a portion of nitric oxide, acquires some peculiar properties, and forms what has been long known by the name of NITROUS ACID.

SECT. I.

OF NITRIC ACID.

NITRIC acid is the result of the full saturation of nitrogen with oxygen. It has been long known in a state more or less pure : the corrosive acid liquor known by the name of Aquafortis, which is an impure and weak nitric acid, had been employed in the arts; and chemists had been acquainted even with the acid in a pure form, before they had any knowledge of its composition. Priestley observed the production of nitric oxide gas in many processes in which the acid was concerned, and the reproduction of the acid when that gas was again mixed with oxygen; and Lavoisier drew the obvious conclusion, that the acid is a compound of these two gases *. But the nature of nitric oxide gas itself was then unknown; and it is to Mr Cavendish that we are indebted for a knowledge of the composition of nitric acid,—that it is a compound of nitrogen and oxygen.

The experiment by which this was established, consisted merely in taking the electric spark for a considerable time in a quantity of atmospheric air confined in a glass

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* Mémoires de l'Acad. des Sciences, 1776, p. 671.

tube 1-10th inch in diameter, over quicksilver. Dr Priestley had observed, that in an experiment of this kind the air was diminished in volume, and an acid appeared to be generated, as infusion of litmus introduced was changed to a red; but the nature of this acid was not ascertained. Mr Cavendish found that it was not carbonic acid, as he had been at first disposed to conjecture, for, on introducing lime-water, it was not rendered milky, though the lime was neutralized. By making the experiment over a solution of potassa, which served to neutralize the acid, he found that it was the nitric acid which had been formed; its smell was obvious, and paper dipt in the solution burnt with deflagration, as it would have done from being dipt in a solution of nitrate of potassa.

Mr Cavendish found that the generation of nitric acid in this experiment was promoted by the addition of a quantity of oxygen gas to the atmospheric air. When five parts of the former and three of the latter were exposed to the action of the electric spark, the mixture almost wholly disappeared. The same result was obtained from a mixture of oxygen and nitrogen in the proportion of seven of the former to three of the latter by measure; with a proportion of oxygen inferior to this, there remained a portion of uncombined nitrogen. In this experiment it cannot be doubted, as Mr Cavendish has remarked, that the nitrogen gas is enabled, by the agency of the electric spark, to enter into chemical combination with the oxygen, and that the nitric acid is the resulting compound *. This combination of oxygen and nitrogen pre-

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* Philosophical Transactions, vol. lxxv. p. 572. vol. lxxviii. 261.

sents the phenomena, somewhat singular, that it takes place very slowly, requiring the constant agency of the electric spark, and that no emission of light, or sensible production of heat, attends it.

The combination of these gases, and the formation of nitric acid, has been effected by presenting them to each other in a different state. A striking experiment of this kind was made by Mr Milner. It consists in passing the vapour of ammonia through an ignited glass or earthen tube containing black oxide of manganese, the oxygen of which in its nascent state combines with the nitrogen of the ammonia, and forms nitric oxide, which by a farther combination with oxygen gives nitric acid *. This experiment was repeated under the direction of Guyton, and with the same result †. Bayen obtained even nitric acid from the decomposition of black oxide of manganese by heat alone, the elastic fluid expelled from it being transmitted through a bent tube containing a solution of potassa; a little nitre was obtained afterwards by evaporation of the liquor ‡, the acid having been probably formed by the combination of the disengaged oxygen in its nascent state, with a small portion of nitrogen, the existence of which has been observed in this metallic oxide.

The composition of nitric acid is likewise established by its analysis. If it be transmitted through an earthen or glass tube, at a red heat, it is converted into oxygen and nitrogen gases: it suffers a similar decomposition, even

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* Philosophical Transactions, vol. lxxix. p. 300.

† Journal de l'Ecole Polytechnique, Cah. iii. p. 332.

‡ Opuscules Chimiques, tom. ii. p. 180.

when combined with potassa or soda: Or, if it be acted on by an inflammable substance or a metal, part of its oxygen is abstracted, it is converted into nitric oxide, which by a farther abstraction of oxygen is reduced to nitrogen; or even in some cases, where the attraction of the substance to oxygen is strong, the decomposition of the acid is complete, and nitrogen gas is evolved.

It has been found difficult to determine with perfect accuracy the proportions in which the elements of nitric acid are combined. From the different experiments of Cavendish, the proportions deduced would be somewhat different, as the acids formed do not appear to have been precisely the same. Taking the experiment which appears most accurate, they would be fixed at 72.2 of oxygen, and 27.8 of nitrogen.

Lavoisier, by experiments on the decomposition of nitrate of potassa by charcoal, and on the combination of oxygen and nitric oxide, made the proportion of oxygen considerably higher; he stated it in the perfect nitric acid at 80 to 20. Mr Davy has sufficiently shewn that Lavoisier's experiments, made at an early period, were liable to fallacies of which he was not aware, and from which he states the proportion of oxygen too high. Mr Davy found it difficult to determine the proportions, and could do it indeed only in an indirect mode: 1st, By the analysis of nitric oxide, determining its composition, then by adding to it oxygen gas, forming a standard nitrous acid, the composition of which was thus known; and, 2dly, By discovering, in an indirect mode too, what quantity of nitric acid this nitrous acid contained. The proportions he states at 70.5 oxygen, 29.5 nitrogen [*]. Though from the mode in which this result was obtained, it cannot, perhaps, be regarded as perfectly accurate, it may be taken as the nearest approximation.

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[*] Researches, p. 38.

Nitric acid cannot be procured in any considerable quantity by the direct combination of its constituent principles. To obtain it, chemists avail themselves of a salt produced in abundance, either naturally, or in some countries by artificial arrangements, the nitre of commerce, and in which the acid exists in combination with potassa. The process consists in adding to this salt a substance which, exerting an attraction to the potassa sufficiently strong to weaken that of the nitric acid, allows it to be expelled by the application of heat. For this purpose, clay, sand, sulphate of iron, and some other substances, have been used; but these not exerting to the potassa an attraction sufficiently powerful, a strong heat is necessary, and part of the nitric acid is lost by its decomposition. The process introduced by Glauber is now, therefore, always followed by chemists, and even when the acid is prepared on a large scale for purposes in the arts. In this the nitrate of potassa is decomposed by sulphuric acid. Three parts by weight of the salt, in coarse powder, are put into a glass retort, and two parts of sulphuric acid are poured upon it by a retort funnel. The retort is placed in a sand bath, and connected with a range of two or three globular receivers, in the last of which a small quantity of water is put, and which is not accurately closed. Heat is applied by the medium of the sand, and is continued as long as any acid drops from the neck of the retort, being raised towards the end nearly to redness. The whole of the acid nearly (amounting to rather less than half the weight of the nitre) condenses in the first receiver, a small portion is condensed in the second or third, and the water the third contains absorbs more effectually any nitrous acid vapour. Towards the end of the process, when the temperature is high, a quantity of permanently elastic fluid is disengaged, which is pure oxygen, and which may be collected by connecting with the last receiver a bent tube, which is made to terminate in the pneumatic trough. The acid which first distils over is of greatest specific gravity. From an experiment by Dr Perceval [*], it appears, that if the product be taken in three portions, the specific gravity of the first is 1.494, of the second 1.485, and of the third 1.442. This is probably owing to the water of the materials being detained at the commencement of the distillation by its affinity to the sulphuric acid; but passing more easily into vapour afterwards as that acid combines with the base of the nitre.

The usual theory of this process, was, that the sulphuric acid exerts a stronger attraction to the potassa of the nitre than the nitric acid, and disengages it, so that by the application of the heat it is volatilized. The just view of the theory is not quite so simple. It was always observed by practical chemists, that it was necessary, in order to obtain the full product of nitric acid, to add considerably more sulphuric acid than was necessary to saturate the quantity of the potassa contained in the nitre. The affinity of the sulphuric acid, therefore, is in this process aided by its quantity, and still more, from the tendency of the nitric acid to volatility, by the heat applied, and by these joint forces, not by a simple elective attraction, the decomposition is effected.

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[*] Transactions of the Irish Academy, vol. iv. p. 37.

The acid, however, is never obtained without a partial decomposition, and hence, although it be nitric acid which exists in the salt, it is always nitrous, or an acid of a yellow colour, more or less deep, that condenses in the receiver. When the heat is first applied, yellow vapours are disengaged, in a short time they become colourless, and continue so for the greater part of the distillation, apparently from the portion of water in the materials being volatilized at the same time, and preventing the decomposition; but towards the end of the process, when the water has entirely distilled over, and the temperature is raised high, a partial decomposition of the nitric acid, disengaged from the materials, takes place; it loses a portion of its oxygen which assumes the elastic form; a quantity of nitrous oxide is thus produced, which combining with the nitric acid, renders it more or less dark coloured, or converts it into nitrous.

A farther process, therefore, is necessary to convert it into nitric acid. It is put into a glass retort, which is connected with a large receiver, containing a little water. Heat is applied by the medium of a water-bath, the nitric oxide is disengaged, taking with it a portion of acid, and forming nitrous acid vapour, which passes into the receiver and is condensed. As this proceeds, the acid in the retort loses its colour, and at length becomes colourless. It is then the proper Nitric Acid.

As the nitre of commerce has very generally a small portion of sea-salt, or muriate of soda, adhering to it, the acid obtained from its decomposition is contaminated by a minute quantity of muriatic acid, and sometimes by a portion of sulphuric acid. When it is to be employed for more delicate chemical purposes, it is necessary that these should be separated, which may be done by dropping into the acid a solution of nitrate of silver as long as it occasions any precipitation. The precipitate is allowed to subside, and the acid, to render it perfectly pure, is poured off, and subjected to a second distillation.

Nitric acid is a colourless transparent fluid, having a peculiar odour, and emitting white vapours when exposed to the atmosphere. It possesses, in an eminent degree, the general acid properties ; it is highly corrosive, and erodes or burns vegetable and animal bodies, tinging them first of a yellow colour ; even when largely diluted with water, its taste is extremely sour, and it instantly reddens the vegetable colours. Its specific gravity, as obtained by the preceding process, is about 155, or from that to 158.

In this state, however, and indeed in any state in which we procure it uncombined with a salifiable base, it is united with water ; nor is there any process by which it can be obtained free from it. It is even difficult to discover what quantity of real acid is contained in an acid of any given specific gravity. Mr Kirwan supposed that the real acid is that contained in nitrate of soda, and from this, by ascertaining what quantity of nitric acid of a certain specific gravity entered into the composition of this salt, he determined what quantity of real acid it contained ; and then by actual experiment what proportions in acids of different specific gravities. The strongest which we can well procure at the temperature of 60, the specific gravity of which is 1.5543, (which however being, as he states, of a yellowish colour, cannot be regarded as pure nitric acid,) contains, according to his estimate, of real acid 73.54 in 100 parts. Though this and the other numbers may be approximations, they cannot be perfectly correct ; for, the position on which they are founded, that the acid in nitrate of soda is without water, cannot be admitted. The following is the table which he has given :

In NITROUS ACID of different Densities, at the Temperature of 60.

100 Parts Sp. Gravity.	Real Acid.	100 Parts Sp. Gravity.	Real Acid.
1,5543	73,54	1,3364	41,91
1,5295	69,86	1,3315	41,18
1,5183	69,12	1,3264	40,44
1,5070	68,39	1,3212	39,71
1,4957	67,65	1,3160	38,97
1,4844	66,92	1,3108	38,34
1,4731	66,18	1,3056	37,60
1,4719	65,45	1,3004	36,77
1,4707	64,71	1,2911	36,03
1,4695	63,98+	1,2812	35,30+
1,4683	63,24	1,2795	34,56
1,4671	62,51	1,2779	33,82
1,4640	61,77	1,2687	33,09
1,4611	61,03	1,2586	32,35
1,4582	60,30	1,2500	31,62
1,4553	59,56	1,2464	30,88
1,4524	58,83	1,2419	30,15
1,4471	58,09	1,2374	29,41
1,4422	57,36	1,2291	28,68
1,4373	56,62	1,2209	27,94
1,4324	55,89	1,2180	27,21+
1,4275	55,15	1,2152	26,47
1,4222	54,12+	1,2033	25,74+
1,4171	53,68	1,2015	25,00
1,4120	52,94	1,1963	24,26
1,4069	52,21	1,1911	23,53
1,4018	51,47	1,1845	22,79
1,3975	50,74	1,1779	22,06
1,3925	50,00	1,1704	21,32
1,3875	49,27	1,1639	20,59
1,3825	48,53	1,1581	19,85
1,3775	47,80	1,1524	19,12
1,3721	47,06	1,1421	18,48
1,3671	46,33	1,1319	17,65+
1,3621	45,59	1,1284	16,91
1,3571	44,86+	1,1241	16,17
1,3521	44,12	1,1165	15,44
1,3468	43,38	1,1111	14,70
1,3417	42,65	1,1040	[illegible]

The Numbers above the Lines drawn across the Tables, were found by Experiments; those under the Lines only by Analogy.

Mr Davy has also given the following table of the quantities of real acid, in acids of certain specific gravities, deduced from a standard acid in the aëriform state; but neither can this be regarded as free from water.

100 Parts Nitric Acid of specific gravity.		True Acid.	Water.
1,5040	contain	91,55	8,45
1,4475		80,39	19,61
1,4285		71,95	28,35
1,3906		62,96	37,04
1,3551		56,80	43,12
1,3186		52,03	47,97
1,3042		49,04	50,96
1,2831		40,04	53,97
1,2090		45,27	54,73 *

Nitric acid, in its highest state of concentration, is congealed by cold, but the part which freezes is not of the same precise strength as that which remains unfrozen. Mr Cavendish remarked, that there is a certain degree of strength at which it freezes with less cold than when it is either stronger or weaker, but the strength of the acids subjected to experiment not being estimated by their specific gravities, scarcely any precise account can be given of the results. The congelation which took place with the least degree of cold, was that where the acid was of such a strength as to dissolve $\frac{418}{1000}$ of its weight of marble, the freezing point of this acid being —2°. When the acid was either stronger or weaker, it required to

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* Researches, p. 41.

freeze it a greater degree of cold, and the part frozen approached nearer that strength than the portion which did not freeze. When of the strength which Mr Cavendish denotes by $\frac{561}{1000}$, it required to be cooled to —41.6; and when so weak as to be at $\frac{276}{1000}$, it did not freeze till cooled to —40.3 *.

Nitric acid is volatilized by heat, and partially decomposed; when exposed to the temperature of ignition, as by passing it through a red-hot earthen tube, it is completely decomposed, and resolved into oxygen and nitrogen gases. It is partially decomposed by light; exposed to the solar rays, it acquires a yellow tinge from the formation of a quantity of nitric oxide, which is retained by the acid, oxygen gas being evolved; and, if exposed sufficiently long, it becomes of a deep yellow. This change is to be ascribed to the chemical agency of light.

Nitric acid has an attraction to water; it attracts it even from the atmosphere, and it combines with it with great facility, the combination being attended with the production of heat from diminution of capacity. If poured on ice or snow, it immediately dissolves it, and there is a considerable production of cold from the sudden liquefaction of the snow or ice. According to Mr Cavendish's observations on the congelation of the acid, this cold should be greatest either when the acid is of considerable strength, or when it is considerably diluted, while there is an intermediate strength where the cold produced cannot exceed —2, as at that point the liquid formed by the acid with the snow will be of that strength that it will freeze at that tempe-

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* Philosophical Transactions, vol. lxxviii. p. 173.

rature; the cold produced must for the same reason be regulated by the proportions. By adding four parts of nitric acid of the full strength, to seven parts of snow, the temperature falls to —30.

This acid is not sensibly affected by any of the simple gases at a moderate temperature. At the temperature of ignition, hydrogen decomposes it by combining with its oxygen. Even at low temperatures, it is, at least partially, decomposed by almost all inflammable substances, which attract a greater or less proportion of its oxygen: thus charcoal decomposes it with rapidity, and if the charcoal be very dry, and the acid highly concentrated, combustion is even produced. Some substances which contain carbon, as the essential oils, are also inflamed by it; it likewise communicates oxygen to sulphur and phosphorus. The metals, too, decompose it, attracting more or less oxygen, and evolving, therefore, nitric oxide, nitrous oxide, or even nitrogen gas: The metallic oxides thus formed from the action of the metals on it, generally remain combined with a portion of it undecomposed.

Nitric acid combines with the alkalis, the earths and metallic oxides; the salts which it forms with these, being named, in conformity to the principles of the new nomenclature, Nitrates. In power of saturation it is inferior to several of the other acids; hence, if this power is to be regarded as a measure of the force of attraction it exerts, that attraction must be less strong; from the state of condensation, however, in which it exists without any accompanying cohesion, it is capable of exerting energetic actions; but its facility of decomposition limits its action, and this, with the tendency of its elements to pass into the elastic state, either pure or combined, render its compounds easily decomposed: Hence the order of attractions which has been assigned to it, and in which it is placed beneath a number of the other acids.

The generic characters of the nitrates, at least of those with alkaline or earthy bases, are a cool penetrating taste, affording oxygen gas at a high temperature, deflagrating at the temperature of ignition with inflammable bodies, and affording white or yellowish vapours with concentrated sulphuric acid. They are all crystallizable.

NITRATE OF POTASSA. This is the well-known Salt, Nitre or Saltpetre: It is produced abundantly by nature in some situations in warm climates. In India it is mixed with the soil at the surface of the earth, and is extracted by washing with water. The solution by evaporation affords the nitre in irregular crystals, and in an impure state; it is purified by a second and third crystallization.

In Europe the circumstances by which the production of nitre is favoured, require to be assisted and regulated by artificial arrangements, and the process for this purpose is carried on extensively in France and Germany. The refuse of vegetables, together with various animal matters, such as blood, and other excrementitious substances, are mixed with carbonate of lime, old plaster, or other materials containing calcareous earth. The mixture is laid in heaps in ditches protected from the rain by sheds, but open at the sides. These are termed nitre beds; the materials are allowed to remain in them for some months, being turned up occasionally to present a new surface to the atmosphere. They are then washed, and a considerable quantity of the salts formed by the union of nitric acid with lime and potassa, are extracted.

The theory of this process, in which nitric acid is formed, was not understood until elucidated by the discoveries of modern chemistry. It was formerly believed, either that the nitric acid existed ready formed in the atmosphere, and was attracted from it by these materials, or that it existed in the animal and vegetable substances, and was extricated from them by the putrefaction. The experiments of Thouvenel, whose memoir on the formation of nitre, presented to the Academy of Sciences, gained the prize offered by the French government, first threw light on the process, by establishing clearly the principal facts connected with it; and the discovery of Mr Cavendish of the composition of nitric acid completed the theory. The following is an outline of the general facts, from the memoir of Messrs Thouvenel.

They imitated the common process, varied it, and examined with attention the influence of different circumstances on the formation of the nitre. Animal and vegetable matters were mixed with calcareous earth, and exposed to the air in large earthen or glass vessels, when nitre was formed. If the calcareous earth was kept out, there was no formation of nitre, not even when either of the fixed alkalis was substituted for it. When magnesia or argillaceous earth was used, the quantity was very inconsiderable; even quicklime did not answer the purpose so well, but in order to obtain the proper effect, it was necessary that it should be in its mild state, or combined with carbonic acid. It was likewise found, that if the putrefying matter was in a separate vessel, and the air arising from it were washed in lime water, or in a solution of caustic alkali, before being brought into contact with the carbonate of lime or other bases, the formation of nitre ceased. Different animal substances produced different quantities of nitre; blood gave most; and the production of it was also different at different periods of putrefaction. The presence of atmospheric air is indispensable to the process, or nearly so, since, when it is excluded, and the vessels contained only the putrid effluvia, no nitre was formed; at the same time if the air was agitated, or frequently renewed, the production was rather lessened. The presence of moisture is likewise favourable to its production, as it is more abundantly formed in damp places, than where the air is dry. Too much humidity, however, is rather hurtful. Lastly, the presence of a quantity of nitre, or of nitrate of lime, already formed, appears to render the farther formation of it at least more rapid. This, however, is only to a certain extent, for after a certain quantity of nitrous salts is formed, the process stops, but if these be extracted by washing, it again commences when the materials are exposed to the air *.

It may be difficult to explain precisely the operation of all these circumstances. In general it may be observed, that during the putrefaction of the animal matter, nitrogen gas is disengaged, which being presented to the oxygen of the atmospheric air in a nascent state, combines with it, and forms the nitric acid. It seems probable

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* Journal de Physique, t. 29. p. 264.

that the vegetable matter, when it is present, not only moderates the putrefaction of the animal matter, but furnishes a quantity of oxygen also, with which the nitrogen combines. The utility of the lime is best explained on the principle of the affinities it exerts to oxygen and nitrogen, in consequence of which it brings them into combination, and attracts and fixes the nitric acid that is formed. The superiority of the carbonate of lime over pure lime, seems to arise from this circumstance, that the pure lime acts too strongly on the animal matter, combines directly with part of it, and resolves the rest into ammonia, while the action of the carbonate is much more mild and slow. The potassa and soda act in the same manner as lime, and are therefore equally unfit for the process of nitrification. The utility of moisture seems owing to its absorbing and detaining in some measure the disengaged gases, and to its diffusing through the materials the nitrous salt when it is formed. Some have imagined that it is decomposed, and furnishes oxygen to the nitrogen of the animal matter; but it has justly been observed, that if this were the case, the presence of atmospheric air would not be necessary, and that during animal putrefaction, nitric acid ought always to be formed.

It appears, then, that the circumstances indispensable for this process, or which are at least more directly concerned in it, are the presence of animal matter, and the action of atmospheric air and of carbonate of lime. Nitrogen gas is discharged from the former, and the lime by a disposing affinity effects its combination with the oxygen of the atmospheric air. There is some reason to believe, that under certain circumstances carbonate of lime alone is able, by its action on the nitrogen and oxygen of the atmosphere, to cause them to combine and form nitric acid; since it has been found that calcareous rocks, at a great height, and at a distance from all animal effluvia, have been encrusted with nitrate of lime. The formation of nitre, however, is always more abundant where animal effluvia are present, and often takes place where all the arrangements of nitre beds are not present. Thus nitre often appears as an efflorescence on the walls of stables, and of old buildings which are in some measure protected from too much humidity.

Experiments appear even to render it probable, that a quantity of potassa is formed in this process which combines with the nitric acid; and the vegetable matter has been supposed to contribute more particularly to its formation, or perhaps it may yield it ready formed. Even this substance or its base, appears to be capable of being elevated in the vapour of the putrefying matter; as well washed chalk, it was ascertained both by Chaptal and Thouvenel, yielded nitre after having been exposed to the effluvia of putrefying substances for some months.

The nitrate of lime, and the nitrate of potassa, which are formed by the process now described, are extracted by washing the materials with water. The water dissolves the salt; a quantity of wood ashes is added, the potassa contained in these decomposes the nitrate of lime, by attracting the nitric acid, and the nitrate of potassa thus formed, together with the quantity of it originally contained in the solution, are obtained by evaporation and crystallization. The salt is at first in a very impure state, being mixed especially with a large quantity of sea-salt or muriate of soda, which appears even to be formed along with the nitre, and always to accompany it. From this it is purified by a second or even a third solution in boiling water, and subsequent crystallization.

A full view of the process of nitrification, particularly in what relates to the practice, was drawn up by Chaptal at a period when the production of nitre was of much importance to France, and published in the Annales de Chimie, tom. xx. p. 308., as well as a new process which was carried into practice, of extracting and refining the nitre. The latter is translated in Nicholson's Journal, 4to, ii. 23.

Nitrate of potassa, according to Kirwan, consists of nitric acid 44, potassa 51.8, and water of composition 4.2.

It crystallizes in six-sided prisms acuminated by six planes, often perforated, and of considerable size, sometimes also in a dodecahedron formed of two six-sided pyramids, joined by their bases; its taste is cool and penetrating; it is soluble in seven parts of water at the temperature of 60, a considerable degree of cold attending its solution, and in an equal weight of boiling water; the latter solution crystallizing upon cooling. In evaporating its solution, it has been ascertained that part of the salt is carried off, probably from its affinity to the water. It melts on the application of a moderate heat, into a transparent fluid, which when cold forms a white semi-transparent mass. If the heat be continued, a partial decomposition of the acid takes place, and the salt is converted into nitrite of potassa, the alkali having still power to retain the nitrous acid by its attraction for it. The oxygen expelled in this stage is nearly pure. By a farther application and increase of the heat, the nitrite is also totally decomposed, not by the mere expulsion of the acid, but by its decomposition; its oxygen and nitrogen are separated from their chemical combination, and pass off in the state of gas; the oxygen therefore which is last disengaged, is less pure than that towards the middle of the process. The decomposition appears to be aided when it is performed in an earthen retort, by the affinity of the alkaline base of the nitre to the earthy matter; and accordingly when the decomposition is complete, the potassa is found in combination with silex, forming a gelatinous solution when water is added to it. It likewise takes place however in a glass retort, but less air is obtained *; in an iron retort the air obtained is less pure. These facts, with regard to the decomposition of nitre by heat, were principally ascertained by Berthollet †. He states the quantity of air obtained at from 550 to 580 cubic inches from one ounce of nitre; Cavallo obtained 750 cubic inches; and Ehrman from 7 to 800.

The action of this salt on inflammable substances has already been considered when treating of deflagration; as its acid is so easily decomposed, and as it contains so large a quantity of oxygen, it is obvious that when exposed to heat with any of these bodies, its oxygen will be yielded to them, and a rapid combustion excited. Accordingly when sulphur or charcoal is mixed with an equal weight of nitre, and thrown into an ignited crucible, the inflammable body is oxygenated, and a large quantity of light and caloric is extricated; the residuum is the product of the oxidated compound with the potassa.

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* Ehrman, Essai d'un Art. de Fusion, p. 23.

† Mémoires de l'Acad. des Sciences, 1781, p. 3.

When it is deflagrated with charcoal, a pure sub-carbonate of potassa is obtained, and this process has been often followed by the chemists, to prepare that salt. When exposed to heat with three parts of the salt named tartar, which consists of potassa and a particular vegetable acid, the tartaric, both acids are decomposed, and the residuum is carbonate of potassa mixed with a quantity of charcoal derived from the tartaric acid. This, as being employed to promote the fusion of earthy and metallic substances, has been named black flux. The white flux, which is merely a sub-carbonate of potassa, is formed by treating in the same way equal parts of nitre and tartar.

On this property of nitrate of potassa is established the composition of gunpowder, which owes to this salt its detonating quality. This powerful agent is composed of 75 parts by weight of nitre, 16 of charcoal, and 9 of sulphur. These are triturated in the gunpowder mills, so as to mix them thoroughly; a small quantity of water being added to keep the powder from flying off in dust, and to lessen the risk of explosion. It is brought at the end of the trituration to the consistence of a thick paste; this, after being dried a little, is pressed through a wire sieve, by which it is granulated, and by causing these grains to rub against each other, in barrels which revolve on their axis, they are rounded and glazed *.

The general theory of the action of gunpowder may be easily understood. The particle of it on which the spark struck by the flint from the steel falls, is immedi-

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* A full account of the process, as carried on in England, is given by Mr Coleman, Philosoph. Magazine, vol. ix.

ately heated to the temperature of ignition, or near to it; the nitre is instantly decomposed, partly from the operation of the heat, and partly from the affinities exerted to its oxygen by the sulphur and charcoal which are equally heated, and with which the oxygen combines. This combination extricates as much caloric as is sufficient to inflame successively, though rapidly, the remaining mass. The cause of the great expansive force of the gunpowder, when inflamed in a confined space, is the sudden production of nitrogen, sulphurous acid, and carbonic acid gases, probably with a quantity of water converted into steam, the elasticity of all of them being greatly augmented by the large quantity of caloric which is also let loose. The influence of the high temperature from the deflagration in augmenting the elasticity, is very well shown in an experiment by Count Rumford, in which gunpowder was fired under the pressure of a great weight. When, by sufficient pressure, the elastic fluid was confined, after having been generated, for a few minutes or even a few seconds, the expansive force it exerted was far from being considerable; some of the carbonic acid, however, must have been absorbed, as Berthollet has remarked, by the potassa in the residual matter, though the effect of this could not be considerable.

From this explanation of its mode of operation, it is obvious, that next to the proper proportion of the ingredients, its power will depend on their proper mixture, especially on the equal diffusion of the nitre. The more finely it is divided, and intimately mixed with the sulphur and charcoal, the combination will be more instantaneous, and consequently the production of the gases from a certain quantity of it, will be greater in a given time, and the expansive force of course augmented. Hence the damage which gunpowder receives from moisture, as the nitre being very soluble in water, is separated more or less from the other ingredients. It is from this cause, too, that the granulation of the powder, though it renders it more convenient for use, weakens its power. Even in the best state of preparation, it appears from Rumford's experiments, that much of the gunpowder fired in a confined space, is thrown out without being sufficiently kindled, to afford the same products. The principal use of the sulphur in gunpowder seems to be, to render it more easily inflamed than it would be did it consist of charcoal and nitre alone.

There is another composition still more powerful than gunpowder, of which nitre is also the principal ingredient. It is named *pulvis fulminans*, or fulminating powder, and is composed of three parts of nitre, two of sub-carbonate of potassa, and one of sulphur triturated thoroughly together. This detonates even when it is not confined, but merely heated. If 10 grains of it be heated on an iron spoon, it first fuses, and in a little longer time explodes with a very loud report. Experiments have shewn that in this experiment the sulphur and potassa first combine and form sulphuret of potassa, since if the mass is removed from the fire as soon as it is fused, it is found to consist of that sulphuret mixed with nitre, and since by triturating sulphuret of potassa with nitre, a similar compound is formed. It is supposed that by the farther continuance and increase of the heat, a quantity of sulphuretted hydrogen gas is produced from the action of the sulphuret on the water present in the mass, and that this instantly combining with the oxygen at the same time expelled from the nitre, sulphurous acid gas and aqueous vapour are suddenly formed, the expansive force of which is augmented, by the large quantity of caloric likewise suddenly extricated. Part of the detonation seems also to be owing to the extrication of the carbonic acid of the carbonate, as, when prepared with potassa that has little carbonic acid combined with it, its detonating power is much less.

Nitre is used principally in the formation of gunpowder, and in the preparation of nitric acid. In a small proportion it is sometimes used to preserve animal matter from putrefaction, and it is employed in the processes of pharmacy and in the practice of medicine.

Nitrate of Soda.—With soda nitric acid combines with facility, and forms a neutral salt, which crystallizes in rhomboidal prisms, and which was therefore formerly termed rhomboidal or cubic nitre. This salt is not found in nature, but is always formed by art, most easily by the direct combination of the acid and alkali. Its taste is cool, penetrating, and somewhat bitter; it slightly attracts moisture from the air; it is soluble in about 3 parts of water at the temperature of 60, and in an equal weight of boiling water, though some have represented it as being scarcely more soluble in hot than in cold water; it is scarcely so fusible as the nitrate of potassa, but is otherwise decomposed by heat in the same manner. It consists, according to Kirwan, of 53.21 of real acid, 40.58 of alkali, and 6.21 of water of composition.

Nitrate of soda acts upon inflammable substances precisely in the same manner that nitrate of potassa does; when deflagrated with charcoal in a proper proportion, its acid is totally destroyed, and the alkali remains combined with carbonic acid. This is one of the easiest methods of obtaining pure soda.

As this salt contains more oxygen than common nitre does, it has been imagined that it would form a more powerful gunpowder. It is affirmed, however, by Vauquelin, that the gunpowder into which it enters is rather less powerful; and were it even more so, it would not be preferable, as it is more apt to attract humidity on keeping.

Nitrate of soda, like that of potassa, is decomposed by sulphuric acid, by clay and siliceous earth, affording nitric acid by distillation. It is likewise decomposed by potassa, which shares its acid with the soda. It is not applied to any useful purpose.

Nitrate of Ammonia.—This salt is likewise the product of art, and is easiest prepared by adding to carbonate of ammonia, nitric acid. It has a cool, bitter taste, is deliquescent, and soluble in two parts of cold water, and in half its weight of boiling water; by the cooling of its solution it crystallizes, the salt obtained being different in its appearance and in the quantity of water it contains, according to the extent of the evaporation and the mode of crystallization. If it be obtained by slow evaporation, at a temperature not exceeding 70, the crystals are tetrahedral prisms, terminated by tetrahedral pyramids. The solution evaporated at a higher temperature, gives an assemblage of indistinct fibrous crystals, containing less water of crystallization; and its solution evaporated fully at 300, forms a compact mass, in which the quantity of water is still less. In all these, the proportion of the acid to the alkali, is, according to Mr Davy, the same. He gives their composition as follows:

Prismatic crystals,	acid 69.5	Ammonia 18.4	Water 12.1
Fibrous Salt	—— 72.5	—— 19.3	—— 8.2
Compact Salt	—— 74.5	—— 19.8	—— 5.7

100 parts of crystallized nitrate of ammonia, by Kirwan's estimate, consist of 23 of alkali, 57 of acid, and 20 of water.

Nitrate of ammonia is decomposed by sulphuric acid, which combines with its alkali, and by the other two alkalis which seize upon its acid.

When this salt is exposed to a moderate heat, it undergoes the watery fusion. The water of crystallization is gradually expelled, and part of the salt is volatilized with it. The greater part, however, remains as a dry white mass; if the heat is increased, it is soon decomposed; and if raised to ignition, is decomposed with a sudden detonation. The cause of this detonation is derived from the peculiar composition of this salt. It consists of nitric acid, which is composed of nitrogen and oxygen, and of ammonia, which is composed of nitrogen and hydrogen. When exposed to heat the acid and alkali are decomposed; the oxygen of the one combines with the hydrogen of the other, and forms aqueous vapour, which is suddenly disengaged with a large quantity of nitrogen gas. Berthollet, by performing the experiment in close vessels, found these to be the products.

Mr Davy, in his researches on nitrous oxide, determined with more accuracy the circumstances of this decomposition. He found that its decomposition with detonation is produced only above 600, and along with nitrogen and watery vapour, nitric oxide and nitrous acid are disengaged. At lower temperatures, it decomposes more slowly, water and nitrous oxide being the products. The different varieties of the salt suffer the same change at different temperatures. The compact salt between 275 and 300 sublimes slowly, without decomposition, or without becoming fluid; at 320 it becomes fluid, sublimes and at the same time decomposes; between 340 and 480 it decomposes rapidly. The prismatic or fibrous salt becomes fluid at temperatures below 300, and between 360 and 400 sublimes without decomposition, nor does it decompose but at temperatures above 450 *. These decompositions are owing to the combination of oxygen and hydrogen, and oxygen and nitrogen, in those proportions which form water and nitrous oxide; and it is from the decomposition of this salt that nitrous oxide is best procured. It is the only use to which it is applied.

Nitrate of Barytes is easily obtained, by disolving either pure barytes or the native carbonate in diluted nitric acid: the solution, by evaporation, crystallizes in octaedrons, or in small brilliant plates: its taste is styptic and pungent: it is not much altered by exposure to the air: when crystallized, it is soluble in 10 or 12 parts of water at 60, and in 3 or 4 parts of boiling water; the latter solution crystallizing on cooling. It is decomposed by heat; little of its acid is expelled in an undecomposed state,

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* Researches, p. 87.

but it is converted into oxygen and nitrogen gases. It detonates but feebly with inflammable bodies. According to Kirwan, it consists of barytes 57, acid 32, and water 11; according to Vauquelin of barytes 50, nitric acid 38, and water 12 *.

NITRATE OF STRONTITES is easily formed, by pouring diluted nitric acid on the native carbonate. The solution, by evaporation, affords crystals, which are either hexaedral pyramids, or octaedrons, with frequently the apex of the pyramid or the angles truncated. This salt is very soluble in water. At 60°, it does not require more than an equal weight; and at 212°, it dissolves in little more than half its weight; the latter solution depositing a confused mass of crystals on cooling. It is deliquescent in a humid atmosphere; and, on the contrary, in a dry atmosphere it effloresces. It is readily decomposed by heat, and gives more nitrous acid vapour than nitrate of barytes decomposed in the same way. It deflagrates feebly, when laid on burning fuel. According to Vauquelin, it is composed of 47.6 of base, 48.4 of acid, and 4 of water.

NITRATE OF LIME.—This salt is generally found in those situations in which nitrate of potassa is formed, and appears to derive its origin from the same process. It has also been said to be obtained from certain mineral waters; but the easiest mode of obtaining it pure, is by the direct combination of its principles. When the solution is evaporated to the consistence of a syrup, it affords slender

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* Journal de l'Ecole Polytech. Cah. III. p. 381.

prismatic crystals. These are very deliquescent; and are soluble in less than an equal weight of water at the temperature of 60, and in still less boiling water. They are also soluble in alkohol. Exposed to heat, they undergo the watery fusion, and are very soon decomposed, the acid being expelled. By having been heated it becomes phosphorescent, and retains this property even when cold. This forms what was termed by chemists Baldwin's Phosphorus. When thrown on burning fuel, it first melts, and afterwards detonates slightly. It consists, when well dried in the air, of 32 of lime, 57.44 of acid, and 10.56 of water.

Nitrate of Magnesia.—This salt is found, along with the nitrates of lime and potassa, in the materials of nitre beds, and is contained in the lixivium they afford. To have it pure, it is prepared by the direct combination of its principles. Its taste is bitter and acrid. Its crystallization is scarcely regular, but exhibits a mass of small needle-like crystals: by spontaneous evaporation, it concretes in quadrangular prisms: it is deliquescent; is soluble in its own weight of water, at a mean temperature, and in half its weight of boiling water: it is also soluble in alkohol. By exposure to heat, it is decomposed: its acid being partly expelled, partly resolved into its constituent principles. The proportions of its principles are 22 of magnesia, 46 of acid, and 22 of water.

Nitrate of Argil.—The solution of argil in nitric acid, becomes gelatinous on evaporation, and soft crystalline scales are formed. This saline matter has generally an excess of acid: its taste is sour and astringent: it is easily soluble in water, and deliquesces on exposure to the air. When exposed to heat, it is decomposed; its acid being expelled without decomposition, the temperature requisite for its expulsion being less than that necessary to decompose it.

The nitrates formed from the remaining earths have been little examined. With Silex, nitric acid does not combine. NITRATE OF ZIRCON is not easily obtained with the acid perfectly neutralized: the solution of the earth in the acid when evaporated, affords a transparent resinous like matter, not easily dried, having an astringent taste. NITRATE OF GLUCINE is very soluble in water, and retains it so strongly that it cannot be crystallized: by evaporation it forms a gelatinous mass, which is very deliquescent. Its taste is sweet and astringent. NITRATE OF ITTRIA can scarcely be crystallized; it assumes a gelatinous consistence by evaporation, and becomes brittle when this jelly cools. Its taste is sweet and astringent.

SECT. II.

OF NITROUS ACID.

IT has already been observed, that in the process for obtaining nitric acid by the decomposition of nitrate of potassa by sulphuric acid, the acid which distils over is always of a yellow colour more or less deep, and that it owes this to the presence of a portion of nitric oxide gas. Hence, by exposing it to heat so as to expel this gas, it becomes colourless, or is converted into nitric acid. The coloured acid has been even longer known to chemists than the colourless; it was denominated Nitrous Acid, a name which was retained in the new nomenclature.

In conformity to the principles of the modern system, which regards a number of the acidifiable bases as capable of existing in two precise states of oxygenizement, forming two distinct acids, nitric and nitrous acids were considered as standing in this relation; the former being the result of the full oxygenation of nitrogen, the latter consisting of nitrogen with a less proportion of oxygen.

There appears, however, every reason to believe, that this view is incorrect, and that nitrous acid is not an immediate compound of oxygen and nitrogen in determinate proportions different from those which constitute nitric acid; but that it is merely nitric acid holding in solution variable quantities of nitric oxide gas. This appears sufficiently from the simple experiment of adding nitric oxide to nitric acid. When we transmit through the liquid nitric acid a stream of nitric oxide gas, it acquires at first a pale straw colour; by continuing the experiment, the yellow becomes more predominant; it gradually deepens, as the nitric oxide is added, to the orange; becomes at length nearly red; it then assumes, by a farther addition, successively, an olive green, a bright green, and a bluish green; and, finally, if the addition of nitric oxide be continued, becomes so saturated with it as to pass into the elastic state, forming a dense, red-coloured vapour. Now, in all these stages of the experiment, there is no precise acid to which the name of Nitrous can be exclusively applied; and the simple view of the process is merely that the different coloured liquids are nitric acid, with different proportions of nitric oxide.

If, indeed, it could be shewn, that when the nitric oxide is absorbed by the nitric acid, it is resolved at once into its elements, which enter into the combination that constitutes nitric acid itself, the theory that nitrous acid is an immediate compound of oxygen and nitrogen, in a certain proportion, might be maintained; though still, instead of being able to establish merely the existence of one acid of this kind, we should be obliged to admit the existence of a number almost indefinite. But there is nothing by which even this view can be established; and the simple, and apparently direct inference from the phenomena is, that nitric acid can dissolve or hold combined nitric oxide from which it acquires colour proportioned to the quantity. The combination appears to be similar to that by which water holds a portion of oxygen or hydrogen dissolved, taking place only with less limitation; and accordingly, the nitric oxide can always again be separated by raising the temperature, carrying with it at the same time a portion of the acid, from the affinity which it has towards it.

The only fact from which the existence of a nitrous acid can be inferred, is, that an acid of this kind, different from the nitric, can be obtained in combination with an alkaline base. Such a nitrite, as this salt is named, is formed by exposing nitrate of potassa or soda to a high temperature: if it be not raised too high, or continued too long, pure oxygen only is disengaged, and an acid remains in combination with the alkali, which when disengaged by a stronger acid has all the characters of nitrous. To this it has been supposed by some chemists the name of Nitrous properly belongs; and it has been imagined even, that it may be of determinate composition. But a different view, in conformity with what appears to be the just theory of the constitution of nitrous acid, may be given. It is not difficult to conceive, that nitric oxide, condensed by the affinity exerted to it by nitric acid, may be so far attracted by an alkali as to be retained in combination, forming a species of ternary compound. Water dissolves nitrous gas very sparingly; but dissolves it much more abundantly when nitric acid is present, the affinity of the acid both to the water and to the oxide co-operating with the weak affinity of the water to the oxide, so as to retain the whole in combination. Though we cannot combine nitric oxide and an alkali alone, there can be little doubt of the existence of an attraction between them, especially as there exists an attraction between the alkalis and nitrous oxide; and this affinity, aided by the attraction of nitric acid to each, may form a species of combination, with probably even various proportions of nitric oxide. This combination, too, may be capable of being formed only in the indirect mode in which it is produced, from both the nitric acid and oxide being in a state of greater condensation than when they are presented to an alkali in a liquid form combined with water. The existence, therefore, of a compound, such as has been described, is no proof of the existence of a specific acid, an immediate compound of oxygen and nitrogen in proportions different from those which constitute nitric acid; nor is there more reason for giving the name of Nitrous Acid to the acid in this compound, than to any of the other acid liquors formed from nitric acid and nitric oxide.

Although, however, there is every reason to believe, that the liquids to which the name of nitrous acid has been given, are solutions of nitric oxide in nitric acid, there are some facts with regard to them which require to be stated.

The nitrous acid obtained by distillation from nitrate of potassa and sulphuric acid, is generally of a pale yellow colour, or does not contain much nitrous oxide. If the heat has been raised very high towards the end of the process, so as to decompose more of the acid then distilling, it is of a deeper yellow; if the materials have contained a very small quantity of any inflammable matter, it is even of a dark orange or red; or if, after it has been produced of a pale colour, a little of any inflammable substance be added to it, the same shades of colour are also produced; or they may be obtained, as has been remarked, from the chemical agency of light, and still more directly by the communication of nitric oxide gas.

Mr Davy, from experiments on this subject, gives the following proportions of the different coloured acids:

Pale yellow,	Real acid, 90.5.	nitric oxide 1.2.	water 8.3.
Bright yell.	—— 88.94.	—— 2.96.	—— 8.10.
Dark orange	—— 86.84.	—— 5.56.	—— 7.6.
Light olive	—— 86.0.	—— 6.45.	—— 7.55.
Dark olive	—— 85.4.	—— 7.1.	—— 7.5.
Bright green	—— 84.8.	—— 7.76.	—— 7.44.
Blue green	—— 84.6.	—— 8.0.	—— 7.4.[*]

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[*] Researches, p. 37.

The changes of colour are likewise dependent on the state of the acid with regard to dilution. If the dark orange-coloured acid be mixed with water, the different shades are produced, with a large quantity of water, blue, with more acid, olive, and bright green. These colours are not permanent; the oxygen loosely dissolved in the water, or imbibed from the atmosphere, oxygenating the nitric oxide, and bringing the whole to the state of nitric acid. Even the concentrated coloured acids, when exposed to the atmosphere, if they are at the same time secluded from light, absorb oxygen and become pale.

The nitric acid, by these combinations with nitric oxide, has its specific gravity diminished; a pale acid of 1.52, when converted into yellow acid, becoming nearly of the specific gravity of 1.51. The combination, as has been stated, may even be carried so far that the acid, saturated with nitrous gas, assumes the elastic form. It is then of a deep red colour, and appears to be permanently elastic, but it cannot easily be subjected to examination, as water absorbs it, and it acts on quicksilver. This nitrous vapour, if formed under different circumstances, is probably likewise of variable composition.

Nitrous acid in its relations to other chemical agents is similar to the nitric acid. It oxidizes in the same manner, and with the same phenomena, inflammable bodies and metals, and combines with the metallic oxides. These combinations are indeed merely those of the nitric acid, as the nitrous oxide is disengaged during the process.

The compounds of nitrous acid, in its different states, with the alkalis or earths, cannot be obtained by direct combination; for when nitrous acid is added to any of these bases, the nitric oxide is either expelled, or, in the course of the evaporation by which the salt is to be obtained, receives oxygen from the atmosphere, so as to afford a nitrate. Some of these compounds can however be obtained in an indirect mode, by a process pointed out by Scheele, that of exposing a nitrate, as that of potassa or soda, to such a heat as will partially decompose the nitric acid, and expel part of its oxygen. The remaining acid with a portion of nitric oxide exist in combination with the alkaline base. Berthollet observed that the nitrate of potassa treated in this way became alkaline, so as to render green the syrup of violet, and that when an acid was poured upon it, effervescence happened, and nitrous acid vapour was disengaged *. These salts are named Nitrites. They have not been particularly examined, and it is not certain if more than the nitrite of potassa, and the nitrite of soda, can be formed. Mr Davy has shewn that the nitrite of ammonia cannot be obtained. The principal character of this order of salts is the one which has been pointed out, that of affording red fumes, or nitrous acid vapour on the addition of an acid. As part of the alkali appears to be in excess when they are formed, they are deliquescent, and render green the vegetable colours. On exposure to the atmosphere, it appears that they absorb oxygen, and return to the state of nitrates.

As the chemical properties and agencies of the nitric and nitrous acids are so much alike, the latter is generally used in the arts, and indeed for most of the purposes to

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* Mémoires de l'Acad. des Sciences, 1781, p. 30.

which the other might be applied, as it is more easily procured. The acid also, for the greater number of purposes for which it is used, must be diluted, and in this dilution it soon passes to the state of nitric. It is extensively employed in several arts, particularly for etching on copper, and in some of the processes of dyeing, as well as in the art of assaying. It is an agent of the first importance in chemistry, from the facility with which it parts with oxygen, and dissolves the metals. It is used in medicine as a tonic. Under the form of vapour, it has been successfully employed to destroy contagion. The *aquafortis* of commerce is a nitric acid diluted, and generally impure from the admixture of muriatic and sulphuric acids. Double *aquafortis* is about half the strength of the common nitrous acid, and single *aquafortis* half the strength of the other.

SECT. III.

OF NITRIC OXIDE.

THIS substance, composed of nitrogen in a lower degree of oxygenizement than nitric acid, and possessed of no acid property, exists when uncombined in the gaseous form. It was first observed by Hales, who took notice of one of its most striking characters, the conversion of it into a red vapour, when mixed with atmospheric air. He knew nothing further, however, of its properties; nor did he recognise it as a distinct substance. Dr Priestley is the proper discoverer of it. He observed its production in the solution of different metals in nitric acid, and he examined likewise its particular chemical properties. He gave it the name of Nitrous Air; and by that, or Nitrous Gas, it has been generally known to chemists. The name is evidently not in conformity to the principles of the modern nomenclature, since the term Nitrous is a generic one, applicable to several compounds; and even the addition of the epithet air or gas cannot render it distinctive or specific, as there are other substances belonging to the genus, or other nitrous compounds, (nitrous oxide, or nitrous acid vapour), to which this may be equally applied. For these reasons it has been proposed to name this compound Nitric Oxide, this distinguishing it from the nitrous oxide, and the final syllable *ic* denoting even a higher degree of oxygenizement, the circumstance which constitutes the difference between them. The name is not perhaps strictly proper, since the syllable *ic* is, in the new nomenclature, appropriated to acids; it is preferable, however, to the vague name Nitrous Gas, and it seems difficult to invent any other less exceptionable.

Nitric oxide cannot be formed by the direct combination of its constituent parts, since, when presented to each other, under the circumstances which cause their intimate combination, they unite in those proportions which form the compound at a higher stage of oxygenizement, nitric acid. But it can be obtained with facility, by bringing substances to act on that acid which partially abstract its oxygen, nitric oxide gas being evolved. In such decompositions, however, which are in general effected by the metals, and by several inflammable bodies, the action is not always limited, so that the oxygen shall be abstracted in that proportion which converts the acid into nitric oxide. Frequently it proceeds farther, and portions of nitrous oxide, and even of nitrogen are evolved. Hence some substances answer better than others, or when made to act on nitric acid more invariably evolve pure nitric oxide.

Of the metals this character belongs to quicksilver and copper. The latter may in general be preferred, not as affording purer nitric oxide, but as the decomposition of the acid goes on with more regularity, and hence the process is more easily conducted, the acid also requires to be diluted to moderate the action. One part of small copper wire, or of copper-filings, is put into a retort; one part of nitric acid, of the usual strength, diluted with 4 or 5 of water, is poured upon it, and a very moderate heat is applied by a taper; or, what has been preferred by other chemists, the nitrous acid is diluted with only an equal part of water, and no heat applied; in either way, an effervescence takes place, which is owing to the decomposition of the acid; the copper attracts a portion of its oxygen, and thus converts it into nitric oxide gas, which rising through the fluid is disengaged, and, by placing the extremity of the neck of the retort beneath an inverted jar filled with water, and placed on the shelf of the pneumatic trough, may be collected. The oxide of copper remains in combination with a portion of the acid, which it attracts without decomposing. The nitric oxide, from the action of copper on nitric acid of the specific gravity, 1.26, according to Mr Davy, seldom contains more than from $\frac{1}{30}$ to $\frac{1}{50}$ of nitrogen, when it has been received through common water: when boiled water has been used, the quantity is not more than $\frac{1}{250}$. That from mercury and nitric acid is nearly of the same purity [*].

This production of nitric oxide in these processes, is a sufficient proof of the nature of its composition. Nitric acid is a compound of oxygen and nitrogen; in being acted on by a metal we find it to be decomposed, and the metal to have acquired oxygen: Of course the nitric oxide, which is the other product of this process, is to be regarded as a compound of oxygen and nitrogen, containing less oxygen than nitric acid.

There are some indirect modes in which nitric oxide is also formed, from which its composition may be inferred. Mr Milner found, that in passing ammonia in the gaseous state, over black oxide of manganese raised to a red heat in a gun barrel, nitrous gas was produced, and might be collected mixed with a portion of undecomposed ammoniacal gas. In this experiment, the oxygen disengaged from the black oxide of manganese, unites with the hydrogen of the ammonia and forms water, and with its nitrogen producing nitric oxide, and the experiment affords an excellent illustration of the nature of this product [†].

The same conclusion as to the composition of nitric oxide is established by its analysis; and by this also the proportions in which its constituent principles are combined have been determined. It is not decomposed by heat alone, not even by the temperature of ignition. By the electric spark, however, it is converted into nitrogen and nitrous acid. It suffers decomposition too from such substances as have a strong attraction to oxygen. Thus, if it be exposed to a mixture of iron-filings and sulphur, moistened with water, or to humid sulphuret of potassa; or if various inflammable or metallic substances, charcoal, pyrophorus, phosphorus, or iron be heated in it, it is converted either into nitrous oxide, by the partial abstraction of its oxygen, or in some of the experiments, particularly in the latter, where heat is applied, the decomposition is complete, and nitrogen gas is the residuum. Mr Davy subjected the greater number of these decompositions to experiment, with the view of determining the proportions of its constituent principles *. By heating charcoal in a measured quantity of the gas, by the aid of a lens, the nitric oxide was converted into nitrogen; and from the quantities of carbonic acid and nitrogen gas produced, he inferred that it consists of 56.5 oxygen, and 43.5 nitrogen. Correcting this estimate by mean calculations derived from the decomposition by pyrophorus, and by hydrogen, he fixed the proportions at 55.95 oxygen and 44.05 nitrogen, or removing the trivial decimal, 56 and 44 †. Lavoisier had inferred that nitric oxide consists of nearly 68 of oxygen and 32 of nitrogen, but his estimate was deduced from an experiment,—the decomposition of nitrate of potassa by charcoal, liable to several sources of error. Mr Davy has shewn that this decomposition is never complete, and that the products are not merely nitrogen and carbonic acid gas, but besides these, variable quantities of nitrous acid, and sometimes of nitrous gas ‡. Inattention to these circumstances, had led Lavoisier to

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[*] Researches, p. 194.

[†] Philosophical Transactions, vol. lxxix. p. 300

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* Researches, p. 122. † Ibid. p. 139. ‡ Ibid. p. 48.

estimate the proportions of oxygen in all the nitrous compounds too high.

Nitric oxide is permanently elastic. It is colourless, and therefore from its rarity invisible. It is rather heavier than atmospheric air, the proportion being nearly as 100 to 92. Its specific gravity was stated by Mr Kirwan at 0.00146. Mr Davy found it to be 0.00136. 100 cubic inches of it weigh 34.3 grains *.

Nitric oxide gas proves extremely deleterious to animal life. Warm-blooded animals die almost immediately on a full inspiration of it, and the irritability of the heart is completely destroyed. Insects which live in several other noxious gases, are quickly killed by immersion in it, and fishes die in water impregnated with it. It proves even noxious to vegetable life, the leaves of a growing plant soon becoming withered in it, and the plant dying.

Nitric oxide gas exposed to distilled water, suffers absorption, amounting, according to Priestley, to about one-tenth of the volume of the water. Mr Davy found that 100 cubic inches of water, which had previously been boiled strongly with the exclusion of atmospheric air, absorbed 11.8 cubic inches of nitric oxide gas; the water did not acquire any peculiar taste †, though Priestley supposed that water, by impregnation with this gas, acquired both taste and odour, probably from the water not being entirely free from loosely combined oxygen, and therefore forming a little nitric acid. Both Priestley and Davy found that the gas is expelled from the water unchanged at a temperature of 212°, and therefore nitric oxide is not, as

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* Researches, p. 49.

† Ibid. p. 143.

Humboldt had affirmed, decomposed by pure water. With common spring water, the absorption appears to be less, but is actually greater, because the gas, as Mr Davy states, suffers decomposition from the atmospheric air held loosely combined in the water; one part of it is absorbed, another part suffers this decomposition by combining with the oxygen of that air, the nitrogen of it is disengaged, and adds to the bulk of the residual gas; but this disengagement of nitrogen is probably rather owing merely to the affinity of the nitric oxide gas to water. Less nitric oxide gas is absorbed by hard water, that is water holding earthy salts in solution, than by water which has no such saline impregnation, as has long been observed in eudiometrical experiments with this gas.

The impregnation of water, however, with some metallic salts, enables it to absorb much larger quantities of nitric oxide gas, and this kind of absorption or combination presents results on which different opinions have been formed by chemists. The fact had been observed by Priestley, that a solution of common green sulphate of iron in water, absorbed a large quantity of nitrous gas, even ten times its bulk, the liquor acquiring a deep olive colour, and at length becoming black *. As green sulphate of iron contains the metal at a minimum of oxidation, and as it is known to have an attraction to more oxygen, so as even to absorb it from the atmosphere, and pass to a salt, the brown or red sulphate, in which the iron is at the maximum of oxidation, it seemed the most probable conjecture with regard to this absorption, that it

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* Experiments on Air, vol. ii. p. 8.

depends rather on a decomposition of the gas, its oxygen being attracted by the salt,—a fact which appeared to be confirmed, as well by the change of colour in the solution, as by another observed by Priestley, that a similar change of colour is produced by the addition of a few drops of nitric acid to the metallic solution; and by one not less striking, and apparently favourable to it, that no absorption of nitric oxide takes place when it is exposed to the solution of the red sulphate, or that in which the attraction to oxygen has been satisfied.

Were this opinion as to the nature of the action of sulphate of iron on nitric oxide gas just, it is obvious that a portion of nitrogen gas should appear, since the oxide is supposed to be decomposed by the abstraction of its oxygen; and it has accordingly been found that nitrogen does exist in the residual air.

Vauquelin and Humboldt, who examined this subject, supposed, however, that the changes were even more complicated than these, and such as give no production of elastic nitrogen. By impregnating a solution of sulphate of iron with nitric oxide, the solution they found reddened the tincture of turnsole; when sulphuric acid was added to it, it gave vapours of nitric acid; and, when saturated with potassa, exhaled ammonia. They concluded, therefore, that in the absorption, not only the nitric oxide, but likewise a portion of the water had been decomposed, the oxygen of the decomposed water combining with the oxygen and nitrogen of the nitric oxide, and forming nitric acid, while the hydrogen of the water unites with another portion of the nitrogen of the oxide, to form the ammonia *. They neglect the operation of the salt of iron, but, in conformity to the supposition that the nitric oxide gas is not merely absorbed, but decomposed, it must be inferred that a portion of its oxygen had been attracted by the oxide of iron, and the nitrogen of this might contribute to the formation of the ammonia.

Mr Davy, in consequence of his researches, has restored the simpler view of this subject; and notwithstanding the apparent force of the facts in support of the opinion that nitric oxide is decomposed by green sulphate of iron, has inferred from his experiments that it is not decomposed, but merely absorbed.

If care be taken to avoid the action of the atmospheric air, by causing the absorption of nitrous gas by the solution of sulphate of iron to take place under mercury, no sensible acidity can be detected in the liquor, and the gas may be recovered unchanged. Mr Davy obtained this result, by placing it under the receiver of an air-pump, and removing the atmospheric pressure, and observed at the same time, that the solution recovers its colour, and is found unaltered in properties. If the solution be exposed to a moderate heat, the gas is also expelled in a very pure state, and the fluid loses its dark colour; but from the alteration of affinities by the temperature, a small quantity of ammonia is formed, which precipitates a little oxide of iron. When, on the other hand, the impregnated solution is not excluded from the atmosphere, oxygen is rapidly absorbed, part of the nitric oxide is thus converted into nitric acid, which re-acts on the oxide of iron in the green

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* Annales de Chimie, t. xxviii. p. 123. 181.

sulphate, and brings the salt to the state of red sulphate; and with the exertion of these affinities, a small quantity of water is decomposed, the hydrogen of which unites with a portion of the nitrogen of the acid, so as to form ammonia. Mr Davy supposes, that it was from not attending to this circumstance that Humboldt and Vauquelin obtained the results from which they inferred, that in the apparent absorption of nitric oxide by sulphate of iron it is always decomposed *.

The residuum of nitrogen, which is observed when nitric oxide has been subjected to the action of the metallic solution, is, according to Davy, merely that which has been produced at the same time in the process by which the nitric oxide is obtained; and hence is derived an easy method of determining the purity of nitric oxide gas; the nitrogen or nitrous oxide mixed with it being left when it is exposed to a solution of green sulphate or muriate of iron.

The absorption of nitric oxide gas by these solutions, Mr Davy supposes owing to an equilibrium of affinity of the elements of the solution to its principles: or it may be conceived owing principally to the affinity of the oxide of iron to oxygen, not sufficient, under the given circumstances, to abstract it from the nitrogen, but sufficient to absorb it with that principle, modified no doubt too by the affinities which may be exerted to the nitrogen itself.

Berthollet, however, still supposes, that in these combinations of nitric oxide gas, a partial decomposition at

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* Researches, p. 152.; Nicholson's Journal, 8vo, vol. i. p. 107.

least takes place, that part of the nitric oxide is converted into nitric acid, and ammonia formed *. But he does not attend to the observation of Davy, that, at a low temperature, these changes arise from the admission of atmospheric air. Yet if they take place, as Mr Davy admits, at a temperature of 200°, it is possible they may do so, though to a less extent, at a low temperature; and it does not appear to have been proved by experiment, that even at a low temperature, the whole of the nitric oxide gas which had been absorbed, is again obtained, by the removal of pressure by the air-pump.

Mr Davy has observed, that some other metallic solutions exert similar actions on nitric oxide gas. A solution of green muriate of iron absorbs it even more rapidly, and to a greater extent, and presents nearly the same phenomena; and it is absorbed with changes of colour, by nitrate of iron, sulphate of tin, and sulphate and muriate of zinc †.

Nitrous gas has no acid properties. Its solution in water, freed from air, does not taste sour, nor does it redden the vegetable colours. Neither does this happen from the introduction of the gas itself, previously washed in water to remove any nitric acid vapour, to the usual vegetable coloured infusions. The colour, however, is always impaired.

Nitric oxide gas is capable of supporting combustion in some substances only, and in them only at an elevated temperature. If a lighted taper be immersed in it, it is extinguished, as is also sulphur introduced in a state of

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* Statics, vol. ii. p. 127. † Researches, p. 190.

inflammation. Phosphorus may be fused or sublimed without burning in it; but if the phosphorus be introduced in a state of active combustion, it then burns with great splendour. Another inflammable substance, pyrophorus, which contains charcoal in a state of extreme division, burns in it even at a low temperature. Charcoal itself, suspended in it in a state of ignition, burns very feebly. It causes hydrogen to burn with a green flame when the mixture is kindled in atmospheric air.

The most important and characteristic property of this gas, is the facility with which it combines with oxygen, while, at the same time, it does not exhibit in this combination the phenomena of combustion. If presented to oxygen gas, they instantly combine together, and a red-coloured vapour is produced, which, if the experiment be made over water, is immediately absorbed, leaving, if the gases be pure, no residuum; no sensible emission of light attends the combination, and so little caloric is rendered sensible, although two gases thus suddenly pass into a dense state, that the vessel scarcely becomes sensibly warm to the hand.

The phenomena are precisely similar when nitric oxide gas is presented to atmospheric air; the combination with the oxygen present takes place with equal facility, red vapours are produced, which are quickly absorbed by water, and if the due proportions (according to Humboldt 85, according to Dalton 72 measures of nitric oxide, to 100 of atmospheric air, have been observed) the nitrogen of the atmospheric air remains pure. As the combination is here less rapid, from the oxygen being in a diluted state, the heat from the combination appears even less considerable than when nitrous gas and oxygen combine.

Although the experiment appears sufficiently simple, it has been found difficult to determine with precision the proportions in which this combination of nitric oxide with oxygen takes place. Priestley found 100 parts of oxygen condensed entirely, or at least to 0.03, by 200 parts, both by measure, of nitrous gas, or 1 part by 2. Lavoisier, in his experiments, found rather a smaller quantity of the nitric oxide gas to be absorbed,—100 parts of oxygen condensing from 165 to 172, or 1 part requiring 1$\frac{7}{8}$. Ingenhouz states the quantity necessary still higher, 100 measures of oxygen requiring, as he affirms, 335 or even 450 parts of nitrous gas; and Scherer states it still higher,—statements, however, evidently erroneous, and arising, in a great measure, from impure nitrous gas having been employed. Humboldt, who engaged in a series of experiments to determine this point, found that 100 of pure oxygen combined with 270 of nitric oxide; from another experiment, he fixed the quantity at 259 *, and as a mean of a number of experiments with atmospheric air, fixed it at 255. Berthollet relates an experiment, from which it appears, that 100 measures of oxygen combined with about 320 of nitric oxide.

The differences in the results of these experiments excluding those of Ingenhouz and Scherer as obviously incorrect, arise from the circumstance, that oxygen and nitric oxide are capable of combining in different proportions, or rather, that although there is one proportion in

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* Annales de Chimie, tom. xxviii. p. 161. 166.

which they are mutually saturated, the compound which results from this proportion is capable of absorbing variable proportions of nitric oxide, and these are materially determined by the circumstances under which the combination takes place.

Thus, if we present the two gases to each other in an exhausted glass globe, or over quicksilver, they combine, and a red or orange vapour is formed, but which remains permanent with very little diminution of volume. From an experiment of this kind, therefore, the proportions in which they combine to saturation cannot be determined, since the nitrous acid vapour retaining the elastic form, variable quantities either of oxygen or of nitric oxide gas may still remain combined with it.

It is necessary, therefore, to admit water, by which the compound will be absorbed, but in doing so we introduce an agent which has an influence on the combination, and, as is immediately to be stated, fixes the proportions, so that, independent of a source of error from the water itself containing atmospheric air, the proportions become various according as it is more or less freely admitted to the mixture. The more largely the mixture of gases at the moment it is made is presented to water, the less oxygen enters into combination with the nitric oxide, probably from the circumstance, that when a narrow surface of water is exposed to the mixture, the absorption is slow, and the progress of the combination continues towards saturation, aided even by the abstraction of the saturated compound as it is formed, while, when the surface is large, it is absorbed as it takes place, and before the proportion in which the nitric oxide is saturated, is fully established.

On the same principle may be explained the facts, that agitation, and even the order in which the gases are presented to each other, influence the results; and from the operation of all these circumstances arises the difficulty of determining with precision the full proportion of oxygen with which nitric oxide can combine.

This property of nitrous gas of combining with oxygen gas where it is not in a state of intimate combination, at every natural temperature, and of forming a compound quickly absorbed by water, has been applied to the purpose of eudiometry, and seems at first view well adapted to it. The combination takes place so rapidly, that the result is immediately obtained, and it requires no complicated apparatus.

The method was introduced by Dr Priestley, and in the way in which he practised it, it was sufficiently simple. One measure, an ounce in general, was filled with the atmospheric air, or whatever air was designed to be submitted to trial, and this was introduced into a jar of 1½ inch in diameter, inverted in water; the same measure of nitrous gas newly prepared was then added to it; and the mixture allowed to stand two minutes. If the diminution of volume is considerable, more nitrous air is added, till the oxygen in the air submitted to examination is saturated. The whole air is then transferred into a glass tube two feet long, and one-third of an inch wide, carefully graduated according to the air measure, and divided into tenths and hundred parts. The space occupied by the residuum can thus be measured, and compared with the quantity of airs mixed, so that the extent of diminution can be perceived; and this gives the comparative purity of the air examined. Fontana made some improvements in this eudiometrical process, principally by rendering all the steps of the operation,—the mixing the gases, the agitation, and the time during which the mixture is allowed to stand, uniform. He used as a measure, too, a glass tube, about two inches long, and one wide, closed at one end, and having a brass plate fixed to the other extremity, in a groove of which a smaller plate slides, so that the included gas is subjected to no pressure, as it is liable to be in a phial with a stopper. The tube in which he mixed the gases is a cylindrical one, three quarters of an inch in diameter, and 18 inches long, graduated into 100 equal parts.

Chemists have always, however, found this method of ascertaining the quantity of oxygen in any air difficult of execution, so as to be perfectly accurate, owing to the number of circumstances, some of them apparently very trivial, by which the results are influenced. These Mr Cavendish pointed out more particularly, at an early period *. He shewed, that if equal measures of the nitrous gas and atmospheric air be mixed in a narrow tube, and immediately agitated, the bulk of the mixture will be in general about one measure; whereas, if the airs are suffered to remain in contact, about one-fourth of a minute before they are shaken, the bulk of the mixture will be hardly less than one measure and two-tenths, and will be very different, according as it is suffered to remain a little more or less before it is shaken. He found also, that the nature of the water over which the experiment

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* Philosophical Transactions, vol. lxxiii. p. 106.

is made, materially influences the result, the diminution being greater with distilled or rain water than with common spring water; owing, no doubt, principally to the expulsion of the nitrogen loosely combined in water which has been exposed to the atmosphere, by the absorption of the nitrous acid, and which, of course, adds to the bulk of the residuum. Another circumstance, having an effect not less important, though more easily obviated, is the order of mixing the gases. When the atmospheric air is put first into the tube, and the nitrous gas added to it, the diminution of volume is always much less than when the common air is added to the nitrous, the diminution being in the one case 1.08, in the other only .90; and the same is observed, as Berthollet has shewn, when pure oxygen is employed, (Statics, vol. ii. p. 145.); though this difference, it is to be remarked, is less considerable when a narrow tube is used for the mixture. With these circumstances others are connected, which depend indeed on the same principle, particularly the length and width of the tube, and the quantities submitted to experiment.

It has also been supposed, that another source of error is in the variable purity of the nitric oxide gas, which, even when obtained by the best processes, may contain 1, 2, or 3 parts of nitrogen or nitrous oxide in 100; and so much has this circumstance been supposed to operate, that Humboldt has proposed a preliminary step in the process, that of ascertaining the purity of the nitric oxide, by exposing a quantity of it to the solution of sulphate of iron, and making allowance for what nitrogen this will shew it to contain. But this is unnecessary. If, indeed, we attempted to ascertain the quantity of oxygen, by adding slowly, in successive quantities, nitrous gas, as long as any diminution took place, stopping at that point, and estimating the quantity of oxygen which had been contained in the air, by the bulk of the residuum, it would be indispensable. But this method is impracticable, at least so as to have any accuracy. In the common method, we merely add to a measure of atmospheric air, such a quantity of nitrous gas as we know is sufficient to saturate and condense all the oxygen it contains; we know what volume the whole would have occupied; we find the volume of the residuum, of course the condensation, and from this we infer the comparative purity of the air, or refer it to a certain standard; and if we have taken care to add as much nitric oxide gas as will condense all the oxygen, no error will arise from its impurity. If, indeed, it be very impure, or contain much nitrogen, this elastic fluid may perhaps retain a small quantity of nitric oxide, or nitrous acid vapour, but the quantity must be very inconsiderable; and in nitric oxide, prepared by any proper process, can never occasion any sensible error. Accordingly, Mr Cavendish has remarked, that atmospheric air, tried "with some nitrous air, which had been debased by the mixture of common air, came out only eighteen thousandths less than when tried with air of the best quality." Berthollet, at the same time, has justly remarked, that though the presence of nitrogen is of no consequence, that of nitrous oxide may give rise to error, as, by agitation with the water, it will be absorbed, and render the apparent diminution of volume greater. But when nitric oxide is prepared by the medium of mercury or copper, it has been proved that no nitrous oxide is evolved.

Though this has usually been considered as the least accurate of any of the eudiometrical methods, Mr Dalton has lately given it a preference to any other, as more expeditious, and equally correct. He has observed, that nitric oxide gas may be combined with oxygen gas, so as to form either nitric acid, or nitrous acid; 36 measures of it uniting with 21 to form the former, and 72 uniting with 21 to form the latter, and the combination in either proportion is determined by the manner of making the experiment. If 100 measures of common air be put to 36 of nitrous gas in a tube 3-10ths of an inch wide, and 5 inches long, after a few minutes the whole will be reduced to 79 or 80 measures, and exhibit no signs of either oxygenous or nitrous gas. If 100 measures of common air be admitted to 72 of nitrous gas in a wide vessel over water, such as to form a thin stratum of air, and an immediate momentary agitation be used, there will, as before, be found 79 or 80 measures of pure azotic gas for a residuum. If in the last experiment less than 72 measures of nitrous gas be used, there will be a residuum containing oxygenous gas; if more, then some residuary nitrous gas will be found *."

The circumstance giving rise to this diversity of combination is the influence of water. The wider the tube or vessel the mixture is made in, and of course the more free the exposure of the gases to water is, the quicker the combination is effected, and the greater the quantity of nitrous acid, and the less of nitric acid is formed; and according to the manner of making the experiment,

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* Manchester Memoirs, new series, vol. i. p. 249.

all the proportions between 36 and 72 of nitrous gas may enter into combination with the oxygen of atmospheric air of the same purity.

In using this gas, therefore, for the purpose of eudiometry, Mr Dalton observes, we must attempt to form nitric acid or nitrous acid wholly, and without a mixture of the other. The former he has found to be most easily and most accurately effected. "In order to this, a narrow tube is necessary; one that is just wide enough to let air pass water, without requiring the tube to be agitated, is best. Let little more nitrous gas than is sufficient to form nitric acid be admitted to the oxygenous gas; let no agitation be used, and as soon as the diminution appears to be over for a moment, let the residuary gas be transferred to another tube, and it will remain without any further diminution of oxygen. Then $\frac{7}{19}$ths of the loss will be due to oxygen." In making the experiment, therefore, on atmospheric air, add 36 measures of nitric oxide gas to 100 of air; conduct the experiment as above directed; ascertain the diminution of volume, and having multiplied this by $\frac{7}{19}$, the product indicates the proportion of oxygen which the air had contained. The tube which Mr Dalton uses is represented, Fig. 44.

Mr Davy proposed another method of applying nitric oxide gas to eudiometry. He found that the solutions of sulphate or muriate of iron, which had been impregnated with nitric oxide, absorbed rapidly the oxygen of atmospheric air. If, therefore, a tube graduated into 100 parts, be introduced into a saturated solution of this kind, the absorption of the oxygen of the contained air immediately commences, and by a slight agitation the process will be completed in a few minutes; the diminution of volume will shew the quantity of oxygen which the air had contained; but it is necessary to observe the progress of the experiment carefully, as, in a short time after the diminution is at a maximum, the volume of the residual gas begins again to be enlarged, from the slow decomposition of the nitrous acid formed during the experiment *. Mr Davy states the diminution obtained in this way at 21 in 100. An apparatus for employing these solutions in eudiometrical experiments has been lately invented by Mr Pepys, the liquid being put into an elastic gum bottle, which is connected by a glass tube, when the experiment is to be made, with a graduated tube containing the air; by pressing the bottle, the liquid is made to act on the air with a degree of compression, which favours the result †. The method is rather complicated for common use, at least when we have others equally accurate and more simple. It affords, however, an accurate instrument for separating other aëriform fluids from each other, and ascertaining their purity, especially when liquids have to be used for these purposes at a high temperature.

Nitric oxide does not combine intimately with either nitrogen or hydrogen gas, at moderate temperatures. If even the electric spark be transmitted through the mixture of it with hydrogen, no inflammation or perceptible diminution is produced ‡. Or, if such a mixture is transmit-

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* Journals of the Royal Institution, p. 45.

† Philosophical Transactions, 1807.

‡ Davy's Researches, p. 136.

ted through an ignited glass tube, it does not, as Berthollet ascertained, suffer decomposition *.

Nitric oxide is likewise incapable of entering into combination with the alkalis, or earths.

SECT. IV.

OF NITROUS OXIDE.

THIS compound is not formed by the combination of its constituent parts, but from the decomposition of nitric oxide or nitric acid, by the action of substances which partially abstract their oxygen. Its existence was discovered by Dr Priestley, who gave it the name of Dephlogisticated Nitrous Air. It was afterwards examined by the associated Dutch Chemists, who named it, in conformity to the principles of the new nomenclature, Gaseous Oxide of Azote. Mr Davy first obtained it in a state of purity, and to him we are indebted for our knowledge of its most singular properties. He gave it the more concise appellation of Nitrous Oxide.

This compound is obtained by various processes, in which nitric oxide or nitric acid is partially decomposed. Dr Priestley procured it by exposing nitric oxide to iron filings moistened with water; the nascent hydrogen disengaged from the decomposition of the water by the iron, attracting part of the oxygen of the nitric oxide, and re-

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* Statics, vol. ii. p. 122.

ducing it to the lower degree of oxygenation, which constitutes nitrous oxide. He found it also to be produced from placing nitric oxide in contact with a humid mixture of iron filings and sulphur, or with the liquid compounds of sulphur with the alkalis, these having the power of abstracting oxygen in a similar manner. Mr Kirwan obtained it by exposing the same substance to sulphuretted hydrogen, and the Dutch Chemists by subjecting it to the action of muriate of tin, of copper dissolved in ammonia, and by passing it over heated sulphur *. In all these cases the nitric oxide gas is diminished in quantity; and its change into nitrous oxide is owing entirely to the partial abstraction of its oxygen, by the substances to which it is exposed.

Nitrous oxide is produced too during the solution of several metals in nitric acid. Dr Priestley observed its disengagement during these solutions of tin, zinc, and iron, mixed with variable quantities of nitric oxide gas and nitrogen gas; its production being probably owing to the decomposition of the water of the acid by the metal, the nascent hydrogen of which, presented to the nitric oxide which arises from the decomposition of part of the acid at the same time, partially abstracts its oxygen, and brings it to the state of nitrous oxide. Mr Davy has accordingly remarked, that the metals which when dissolved in a diluted acid, do not decompose its water, as mercury, lead, bismuth, and antimony, give out only nitric oxide, with, in some of them at least, portions of nitrogen. Hence also nitrous oxide is produced, as the Dutch Che-

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* Journal de Physique, t. xliii. p. 324.

mists remarked, during the solution of iron or zinc in mixed sulphuric and nitric, or muriatic and nitric acids.

By all these processes, however, it is obtained in an impure state, being mixed with variable quantities of nitrogen and nitric oxide gases, from which it is not easily separated. It is disengaged of nearly perfect purity in the decomposition of nitrate of ammonia, by heat. The production of it in this case, had been observed by Berthollet and afterwards by the Dutch Chemists, but the various circumstances relating to it have been determined with more accuracy by Mr Davy, so as to enable us to produce this gas in greatest purity, and with perfect certainty.

The nitrate of ammonia crystallizes under different forms, according to the extent of evaporation to which its solution has been carried. One variety of it is in the form of a fibrous mass, composed of prismatic crystals; another, from a greater evaporation, is dry and compact. These are decomposed at different temperatures. The compact at temperatures between 275° and 300°, sublimes without decomposition; at 320° it becomes fluid, is partly sublimed, and partly decomposed; between 340° and 480° it decomposes with rapidity. The fibrous is not decomposed below 400°; above 450° its decomposition takes place. In both cases water and nitrous oxide are the sole products. At higher temperatures other affinities are exerted. At 600° the decomposition becomes rapid, a luminous appearance is produced in the retort, and the gases evolved are nitric oxide, nitrous oxide, and nitrogen, mixed in variable quantities. When the temperature is raised a little higher, as to 700° or 800°, an explosion happens, and the products are water, nitrous acid, nitric oxide, and nitrogen gas *.

To procure nitrous oxide gas, then, any quantity of nitrate of ammonia, either compact or fibrous, (the latter, according to Mr Davy, being preferable, as sustaining less loss by sublimation, before its decomposition commences), is put into a tubulated glass retort, and is quickly raised to the requisite temperature, taking care not to exceed 500°, and, in particular, not to raise it so high as to produce the luminous appearance in the retort; this regulation of temperature is easily obtained by the manageable heat of an Argand's lamp. The nitrous oxide, with watery vapour, are disengaged; the latter condenses in the neck of the retort; the former is received over water, as it is not immediately much absorbed; it is generally white, and a little opaque, from a small portion of the nitrate of ammonia being volatilized; but this is soon absorbed by the water over which the gas is received; and when it is prepared for the purpose of respiration, it should be allowed to remain an hour at least in contact with water, to deposite this, as well as a small quantity of acid which is suspended in it. From 100 grains of compact nitrate of ammonia, about 85 cubic inches of nitrous oxide gas are obtained. One pound gives 4.25 cubic feet; while one pound of the fibrous salt gives nearly 5 cubic feet †.

The theory of the production of this gas by this process, presents a very striking instance of a nice adjustment of affinities. Nitric acid is a compound of oxygen and nitrogen; ammonia, a compound of hydrogen and nitrogen;

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* Davy's Researches, p. 112. † Ibid. p. 121.

the solid salt, therefore, consists of oxygen, nitrogen, and hydrogen, the affinities of which, at a moderate temperature, are balanced so as to form the binary combinations which constitute the acid and alkali. But when the temperature is considerably elevated, the disposition of these elements, to assume the elastic form, subverts these affinities, and others are exerted, so as to combine them in different modes and proportions; the hydrogen of the ammonia combines with as much of the oxygen of the acid as saturates it, and forms water; and the remaining oxygen of the acid combining with the nitrogen of the acid, and the nitrogen of the ammonia, forms nitrous oxide. The proof that this theory is just, is, that none of the simple elements are evolved during the decomposition: nitrous oxide and water are the only products, and the elements of the salt must therefore necessarily have been combined in this manner for their formation. At a still higher temperature, other forces are exerted. It appears from the experiments of Mr Davy, that nitrous oxide is decomposed by the heat of ignition, as by passing it through a red-hot glass-tube: it is converted into nitrous acid vapour, and a gas analogous to atmospheric air, or composed of oxygen and nitrogen, loosely combined. Hence, when the temperature of the nitrate of ammonia is raised near to ignition, nitrous oxide can either not be formed, or if it be, is immediately decomposed, and resolved into these or similar products, varying probably according to the temperature: nitrous acid and water are formed, and a portion of nitrogen remaining after these combinations, is evolved undecomposed. As nitric acid is likewise decomposed at a state of high ignition, it is not improbable, that, at this temperature, nitrate of ammonia would be resolved into water, oxygen, and nitrogen.

From experiments on the formation of this gas, in the process now described, Mr Davy inferred, that it is composed of 62.4 of nitrogen, with 37.6 of oxygen. This method of determining its composition, supposing a precise knowledge of the composition of several other substances, of water, nitric acid, ammonia, and nitrate of ammonia, is obviously liable to sources of error, yet it corresponds very nearly to the determination by analysis, which is more direct, and probably more accurate. Its analysis can be effected in various modes. When mixed with hydrogen gas, the quantity of hydrogen exceeding very little that of nitrous oxide, the mixture detonates on the introduction of the electric spark, and the products are water and nitrogen gas; the composition of water being known, it is easy to determine what proportion of oxygen, derived of course from the nitrous oxide, had been spent in its formation, by the quantity of hydrogen that had been consumed; and as the remaining product is pure nitrogen, the proportions of these elements in the nitrous oxide may be determined. From this analysis, Mr Davy fixes them at 63.5 nitrogen, and 36.5 oxygen *. From its analysis by charcoal, at a high temperature, the products being carbonic acid and nitrogen, he states them in one experiment at 63 nitrogen, 37 oxygen, in another at 64, and 38. Taking the mean of the most accurate experiments he made, nitrous oxide may be said to consist of 63.3 nitrogen, and 36.7 oxygen; or, disregarding decimals, 63 and 37 †.

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* Researches, p. 291. † Ibid. p. 325.

With this the estimation of its composition by the Dutch Chemists agrees surprisingly, as they were not aware of some circumstances by which it is influenced :, the proportions they give are 62.5 nitrogen, and 37.5 oxygen *.

Nitrous oxide is permanently elastic. Its specific gravity, in its gaseous state, is 1.985, and to that of atmospheric air as 161 to 100 ; 100 cubic inches weigh 50.1 grains †. Its taste is distinctly sweetish, which is felt when it is respired. Its odour is very faint.

This gas is absorbed by water, the atmospheric air of the water being expelled by it ; the water, at a mean temperature, and under atmospheric pressure, takes up about half its bulk ; on boiling the solution, the gas is given out unchanged ; the solution has a sweetish taste, and a slight odour, not disagreeable ; neither it nor the gas changes the vegetable colours.

Nitrous oxide gas suffers no diminution of volume, nor any change of properties, when mixed with oxygen, nitrogen, or hydrogen gas. At ignition, it detonates with hydrogen, as has been already stated. It is even decomposed alone at a high temperature, transmitting the electric spark through it, or passing it through an ignited earthen tube, converting it into nitrous acid, and oxygen and nitrogen gases.

A distinguishing property of which it is possessed is, that of supporting combustion. A lighted taper burns in it with an enlarged and bright flame, nearly as it does in oxygen gas ; phosphorus with a dazzling white light ;

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* Journal de Physique, tom. xliii. p. 331.

† Researches, p. 95.

sulphur with a vivid rose-coloured flame; and iron-wire with corruscations. One peculiarity exists with regard to these experiments, that the inflammable bodies require to be raised to a higher temperature, to burn in nitrous oxide gas, than they do to burn either in oxygen gas or in atmospheric air. If sulphur be burning with a pale blue flame, on introducing it into nitrous oxide, it is extinguished. It is only when the temperature has been previously raised, to cause it to burn with the mixed blue and white, that it continues to burn, when immersed in this gas; phosphorus, which burns in atmospheric air at 40° or 50°, does not burn in nitrous oxide gas but when the temperature is above 212°; and charcoal, and the compound inflammables, require all of them to be in a state of high ignition for this combustion. During these combustions, a portion of nitrous acid is almost always produced, along with the product of the oxygenizement of the combustible body *.

But the most singular property of this gas, is displayed in its action on the animal system, when received by respiration. It had always been supposed to be noxious to life. Dr Priestley found, that an animal confined in it is soon killed; and the Dutch Chemists made similar experiments on birds with the same result, and concluded that it is highly deleterious, from a theory they had formed of its agency, that it is incapable of affording its oxygen to any substance but hydrogen, and that, therefore, it is unfit for abstracting the carbon of the blood, the principal office performed by the air in respiration †.

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* Researches, p. 322.

† Journal de Physique, tom. xliii. p. 329. 332.

The attention of Mr Davy having been directed to the action of this gas on the system, by a very vague hypothesis of it being the principle of contagion, he had breathed it repeatedly mixed with oxygen gas or atmospheric air, without observing from it any particular effect; at length, having obtained it in a state of purity, he resolved to breathe it undiluted, and thus discovered its very singular powers. It is the most powerful stimulant that can operate on the human frame, producing the highest state of excitement both of body and mind, with sensations of the most singular nature, but extremely various in different individuals. The following is the description of the effects Mr Davy experienced from it the first time he breathed it pure, and in sufficient quantity :

" Having previously closed my nostrils and exhausted my lungs, I breathed four quarts of nitrous oxide from and into a silk bag. The first feelings were similar to those produced in the last experiment; but in less than half a minute, the respiration being continued, they diminished gradually, and were succeeded by a sensation analogous to gentle pressure on all the muscles, attended by an highly pleasurable thrilling, particularly in the chest and the extremities. The objects around me became dazzling, and my hearing more acute. Towards the last inspirations, the thrilling increased, the sense of muscular power became greater, and at last an irresistible propensity to action was indulged in ; I recollect but indistinctly what followed ; I know that my motions were various and violent.

" These effects soon ceased after respiration. In ten minutes I had recovered my natural state of mind. The thrilling in the extremities continued longer than the other sensations. This experiment was made in the morning; no languor or exhaustion was consequent, my feelings throughout the day were as usual, and I passed the night in undisturbed repose *."

The same effects were experienced by others, varying, however, in combination and intensity, as might be expected; of these, different relations have been given in Mr Davy's publication. One who has not experienced them, will perhaps be disposed to regard them as exaggerated; but a single trial is generally sufficient to dissipate this doubt. Every precaution, too, has been taken, to guard against the influence of imagination, by substituting sometimes, for example, without the knowledge of the person who was to respire it, atmospheric air. On some individuals, the effects produced have been unpleasant and depressing, sometimes convulsions and other nervous symptoms have been occasioned by it; others have experienced the peculiar effects on the intellectual functions, the crowding of indistinct ideas, and the irresistible propensity to muscular exertion, without the sensation of pleasure which generally arises from it; and in some individuals it has had no sensible effect whatever, even when they have respired it pure, and in considerable quantity. In the same individual, too, they are very different, at different times. The violent operation of it generally ceases in five or six minutes after ceasing to respire it, though sometimes a degree of exhilaration, and propensity to motion, continue for several hours. The quantity of the gas which requires to be respired to produce the full effect, is from

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* Researches, p. 457—8.

4 to 9 or 10 quarts; and it is more powerful when breathed pure, than when diluted with atmospheric air or hydrogen gas. Its operation appears generally in a minute or two. Mr Davy has been able to respire it for 4½ minutes; and some individuals for five minutes. The larger warm-blooded animals confined in it die generally in five or six minutes; the smaller in one or two minutes. It previously produces in them, at least frequently, exciting effects; they become convulsed, and soon insensible; and in some, the insensibility is induced at first. They live, however, in general, twice as long as in hydrogen gas or under water; the lungs are inflamed; the blood of a purple-red colour; and the muscles inirritable. Amphibious animals are affected in a similar manner, but live rather longer. Fishes put into water impregnated with it are soon affected, and die in fifteen or twenty minutes. And winged insects soon become motionless in the gas, and are killed in no long time.

It is not the least of the singularities in the operation of this agent, that the excitement it produces is not followed by languor or debility. No law with regard to the living system seems more general and invariable, than that when increased action is excited by any agent, it is followed, when the excitement passes off, by a proportional degree of lassitude and debility. Nitrous oxide furnishes a very striking exception. Notwithstanding the high exhilaration it produces, this is not followed by any marked exhaustion, but is reduced merely to that state of the system which existed at its commencement, leaving, even for a time, alacrity and pleasant feelings, as has been ascertained by Mr Davy, by experiments made on purpose to determine this point [*]. This I have also repeatedly experienced.

Mr Davy examined the changes which the gas suffered in respiration, with the view of illustrating the nature of the agency it exerts. He found, that after it had been breathed for some time, a great part of it is absorbed, and the residual gas is chiefly nitrogen; and that when exposed to blood, it is in part absorbed, and the residual air is in this case also chiefly nitrogen,—changes probably owing in part to an immediate absorption of the nitrous oxide, and partly to its decomposition, and the abstraction of its oxygen by blood; though Mr Davy inclined to the supposition, that the nitrous oxide is absorbed only, and not decomposed, the nitrogen which appeared being evolved, he supposes, from the blood [†]. The actual consumption of the gas, so as to produce the full exciting effects, does not appear to exceed a pint.

It would be in vain, in the present imperfect state of our knowledge of animal physiology, to speculate on the nature of the agency exerted by nitrous oxide on the living system. "It would be easy," Mr Davy observed, "to form theories referring the action of blood impregnated with nitrous oxide to its power of supplying the nervous and muscular fibre with such proportions of condensed nitrogen, oxygen, light or etherial fluid as enabled them more rapidly to pass through those changes which constitute their life: but such theories would be only collections of terms derived from known phenomena, and applied by loose analogies of language to unknown things [‡]."

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[*] Researches, p. 484. 542. [†] Ibid. p. 415. [‡] Ibid. p. 449.

Nitrous oxide is capable of forming combinations with the alkalis. These combinations cannot be effected by presenting it to them, either in the dry state, or when they are dissolved in water, but take place when the nitrous oxide is in its nascent state. The following is the process by which Mr Davy effected this combination. A portion of a salt formed of potassa with the sulphurous acid, the sulphite of potassa, having a considerable quantity of pure potassa intimately mixed with it, was exposed over mercury to nitric oxide gas. The sulphurous acid in the sulphite of potassa having an attraction to oxygen, decomposes this gas by partially attracting its oxygen, and thus converts it into nitrous oxide. This, as it is formed, is attracted by the excess of pure potassa present; the sulphurous acid, by its farther oxygenizement, being converted into sulphuric acid, this acid remains united with another portion of potassa, forming sulphate of potassa. These two, the sulphate of potassa, and the compound of nitrous oxide with potassa, were in a great measure separated from each other by solution, evaporation and crystallization, at a low temperature. The new compound consisted, as nearly as Mr Davy could estimate, of about 3 of alkali and 1 of nitrous oxide by weight. It had the following properties: its taste was caustic, and possessed of a pungency different from either potassa or carbonate of potassa. It rendered vegetable blues green, which might probably depend upon the carbonate of potassa mixed with it. Pulverized charcoal mingled with a few grains of it, and inflamed, burnt with slight scintillations; projected into zinc in a state of fusion, a slight inflammation was produced. When either sulphuric, muriatic or nitric acid was introduced to it under mercury, it gave out nitrous oxide mingled with a little carbonic acid. When carbonic acid was thrown into a solution of it in water, gas was disengaged, which was nitrous oxide; a fact which shews the weak force by which the nitrous oxide is retained in combination with the alkali [*].

A combination of nitrous oxide with soda was effected by a similar process. The gas did not appear to be absorbed so largely as by potassa. Cast on zinc in fusion, it burnt with a white flame. Heated to 400° or 500°, it gave out nitrous oxide rapidly [†].

By following the same process with ammonia, lime, and strontites, no combination with the nitrous oxide was effected. Some other indirect modes, Mr Davy supposes, would be effectual. The combinations of nitrous oxide with alkaline or earthy bases may be denominated Nitroxides.

Nitrous oxide gas is absorbed by a number of inflammable liquids, and in greater quantity than by water. Alkohol at 52 degrees absorbs more than its bulk; acquires a sweet taste, but in its other physical properties is not altered. The gas is expelled at the temperature of ebullition, and likewise by the combination of the impregnated alkohol with water. The absorption by ether, and the results of it are similar. The essential oils absorb it in still larger quantity, as do also the fixed oils, and from both it is expelled unaltered, by the application of heat [‡].

Berthollet gives the following view of the difference in the constitution of the two oxides of nitrogen, nitrous oxide, which we have considered, and nitric oxide, of which the history is next to be given. The specific gravity of nitrous oxide is greater than that of nitric oxide; hence the elements have suffered a greater condensation in their combination, or the oxygen, though in smaller proportion, is more condensed, because it experiences a stronger action from the nitrogen. These circumstances, says Berthollet, account for the characteristic properties of nitrous oxide, which may be reduced to the two following heads *.

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[*] Researches, p. 262. [†] Ibid. p. 268. [‡] Ibid. p. 240.

1st, The oxygen being subjected to a more powerful affinity than in the nitrous gas, it must offer more resistance to the action of the substances which tend to combine with it, while the constitution of the gaseous oxide of azote (nitrous oxide) is not excited to change; in fact, the gaseous oxide of azote neither burns charcoal, nor sulphur, nor even phosphorus, which have not been raised to a high temperature: it cannot support respiration without difficulty, although the oxygen is in greater proportion in it than in atmospheric air: I have found that it was not changed by the action of a moistened mixture of sulphur and iron-filings, to which I left it exposed for a long time, and which entirely decomposes nitrous gas: it is therefore certain that it resists decomposition at a low temperature much more than nitrous gas.

" 2d, When it experiences the action of heat, on the contrary, it is decomposed more easily than nitrous gas, because the expansion which is the effect of it tends to restore the two gases which compose it, and which are con-

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* Chemical Statics, vol. ii. p. 135.

densed in it, to their natural state, while this expansion has little effect on nitrous gas whose two elements are not much condensed: by it the elements of the gaseous oxide of azote are divided; one part resumes the state of nitrous gas; the other part is reduced into oxygen gas and azote gas, nearly in the proportions of atmospheric air: the continued action of electricity produces the same change, as well as several other circumstances."

CHAP. II.

OF SULPHURIC ACID, AND ITS BASE.

IT was known to the Alchemists, that from certain metallic salts which either exist native, or which can be formed by an easy process from certain metallic ores, a strong acid could be extracted by the process of distillation. These salts had been named Vitriols; and this acid being of great density, and having from this somewhat of an oily appearance, had received the name of Oil of Vitriol. The more correct appellation of Vitriolic Acid was afterwards given to it. In the progress of chemical researches it was discovered, that there exists a peculiar relation between this acid and sulphur, and it was at length demonstrated that this inflammable substance is its base. It was therefore named Sulphuric Acid. It is the product of the full saturation of sulphur with oxygen. Another acid is formed, from a smaller proportion of oxygen being combined with the base, which, in conformity to the principles of the modern nomenclature, is named Sulphurous Acid. Besides these, sulphur combines with hydrogen with perhaps a portion of oxygen, and it forms another series of compounds, either pure or combined with oxygen and hydrogen, with the alkalis and earths. The chemical history of these combinations is to be given in this chapter, beginning with that of the base.

SECT. I.

OF SULPHUR.

Though in conformity to the principles of arrangement, we have pointed out sulphur as the base of sulphuric acid, it is not from this acid that it is procured. It exists in large quantity in the mineral kingdom, both in a pure and a combined state. Native sulphur occurs in different forms; the greater part of it is a volcanic production, but it is also found imbedded in gypsum and limestone, and sometimes, though in smaller quantity, in veins which traverse primary rocks. The sulphur of commerce is generally of volcanic origin, and the greater part of what is imported into this country is the produce of Sicily and Italy.

Sulphur also exists in large quantity combined with some of the metals, particularly with iron, copper, and lead; and it is sometimes extracted in the working of these ores. At the Parys mine in Anglesea, in working the copper pyrites, the sulphur volatilized in the roasting is collected in a chamber, connected by flues with the furnace in which the roasting is performed, and is afterwards purified by melting.

It exists in other states of combination in many mineral substances. It is also a constituent principle of organized matter. In the slow spontaneous decomposition of some kinds of vegetable matter, especially of the plants named cruciform, it is sometimes deposited. Deyeux found, that in extracting, by the usual process, a fecula from the roots of the dock, a considerable quantity of sulphur is mixed with it, which could be separated by sublimation. He also found, that it could be extracted from the root of the horse-radish *. In animal substances it is still more common, and in larger quantity, as is demonstrated by its evolution in combination with hydrogen during their putrefaction or decomposition by heat.

The sulphur of commerce not being perfectly pure, it is purified, especially for medicinal use, by sublimation in close vessels. It then exists in the form of a light powder. The substance named *Sulphur vivum* appears to be the residuum of this sublimation; and Roll sulphur is the common sulphur, generally impure, melted, and run into cylindrical moulds.

Sulphur, when solid, is brittle, and breaks even from the heat of the hand when grasped for a short time, owing probably to its imperfect conducting power, whence the expansion is not equally propagated through the mass. By friction, it becomes electrical. When rubbed, its peculiar odour is also more perceptible. Though of a yellow colour when in mass, yet, when precipitated from some of its combinations, as from its combination with liquid potassa by an acid, in a state of extreme mechanical division, it is nearly white. This whiteness of precipitated sulphur has, however, been supposed to be owing to its combination with a portion of water, a supposition that appears to be proved by the whiteness which is also acquired by sulphur when it is sublimed into a vessel filled with watery vapour, or when water is dropped on it melted. The specific gravity of sulphur is 199.

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* Journal de Physique, 1781, p. 242.

Sulphur is fused by heat. According to Bergman, this takes place at about 224 of Fahrenheit; while in fusion it has a red colour. By slow cooling, it may be crystallized. Its crystallization in needles may often be perceived in breaking a roll of sulphur, and it can be effected without difficulty by the process given by Rouelle, that of melting sulphur, allowing it to cool until it becomes solid to the thickness of one half the mass, then pouring out the remaining liquid sulphur, when the cavity is found lined with needle-like crystals. When dissolved in alkohol, or in essential oils, on long standing, it is deposited in minute crystals, which Pelletier has remarked approach in form to some of the varieties of native sulphur.

A singular phenomenon is presented in the action of heat upon sulphur. When in perfect fusion, if the application of the heat be continued, instead of remaining fluid, and acquiring even more tenuity, until it pass as the heat rises to the state of vapour, it suffers the opposite change, becomes thick and viscid, and this thickness augments for a range of temperature of 200 degrees. This phenomenon has been examined with attention by Dr Irvine *junior* *. He finds, that while the liquefaction of sulphur takes place at about 226° of Fahrenheit, the thickening begins at 320°, and continues, and even increases to 530 or 550, at which temperature copious fumes arise. It can be repeated any number of times upon the same mass of sulphur, and is regularly followed by the diminution of the thickness on the removal of the high temperature. On pouring this viscid matter into water, it remains for a while soft and tough, and even when solid retains a degree of tenacity. Impressions can be taken by applying it to a mold, and these form what have been named Sulphur Casts.

This change had been ascribed to oxidizement; and this viscid or ductile matter had by some chemists been supposed to be an oxide of sulphur. Dr Irvine found, however, that the unrestrained or the difficult access of the air had no effect on the result; and that it appeared to depend entirely on the agency of caloric, as is indeed evident from the liquidity being recovered merely by reducing the temperature. This thickening of the sulphur, as the temperature rises, he found, was not accompanied, as perhaps might have been expected, with contraction; for, on cooling sulphur from the temperature of 400, it continued contracting until it reached 226, its melting point, when, in congealing, it expanded considerably.

Sulphur is also volatilized by heat, at nearly the same temperature as that at which it melts. It condenses again unchanged; or at least with only a slight acidity from the action of the air of the vessel. At a temperature very little elevated, or, as has been stated, at 300 nearly, it combines with oxygen, and presents the phenomena of combustion. It gives a pale blue flame, a considerable quantity of heat is rendered sensible, and vapours are disengaged extremely suffocating and pungent. At a higher temperature, as that of full ignition, it burns with a white flame. In oxygen gas, the light it emits is white, with a shade of blue.

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* Chemical Essays, p. 475.

Sulphur was regarded as a simple substance. The younger Berthollet, however, two years ago, stated some experiments, from which he inferred that it contains hydrogen. It was known, that, by causing sulphur to act on charcoal at a red heat, a peculiar product is obtained, which Lampadius, who first observed it, regarded as a compound of sulphur and hydrogen, but which Clement and Desormes, who afterwards examined it, concluded is a compound of sulphur and carbon. Berthollet examined the circumstances of this experiment: he obtained different products, partly gaseous and partly liquid; and all these he found reason to believe are compounds of sulphur and hydrogen. Hydrogen, therefore, must exist either in charcoal, in sulphur, or in both. The latter conclusion is that which Berthollet drew; and the existence of hydrogen, more particularly in sulphur, he considered as established by the following experiments: 1st, He caused sulphur to pass through a coated glass tube, heated to whiteness, and obtained slight traces of sulphuretted hydrogen. 2d, He formed metallic sulphurets, performing the experiment in an earthen retort, and, after taking every precaution to avoid any source of uncertainty, he obtained sulphuretted hydrogen: the metals he used were iron, copper, and mercury; the last afforded the largest quantity. 3d, He repeated an experiment of Priestley's, passing water in vapour over melted sulphur, and obtaining sulphuretted hydrogen. He satisfied himself that the water had not been decomposed, for he found no trace of acid; it had served therefore only to disengage the hydrogen from the sulphur *.

Lately, Mr Davy has inferred, from experiments on sulphur, by galvanism, and by the action of potassium, that it is a triple compound of oxygen, hydrogen, and a peculiar base.

The result of the oxygenation of sulphur is its acidification, two acids, as has been remarked, being produced from the different proportions of oxygen with which the sulphur combines. The one which contains the smaller proportion of oxygen, is, in conformity to the principles of the new nomenclature, named the *Sulphurous* acid, the other the *Sulphuric*. The former principally is produced in the slow or imperfect combustion of sulphur; it exists in the gaseous form, and constitutes the suffocating and pungent fumes which arise from burning sulphur. The other is formed, in larger quantity at least, in the combustion of sulphur at a high temperature, or in oxygen gas, though a portion of sulphurous acid is always formed with it. It is little volatile, and can be obtained in a much more concentrated state than the other. The sulphuric acid, from the analysis of it by Mr Chenevix, appears to be composed of 61.5 parts of sulphur, and 38.5 of oxygen; the sulphurous has been found by Dr Thomson to consist of 68 sulphur and 32 oxygen.

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* Journal de Physique, April 1807.

SECT. II.

OF SULPHURIC ACID.

To obtain this acid different processes have been employed. Formerly, I have remarked, it was procured from sulphate of iron; this salt, which can be prepared at a low price, by the decomposition of native sulphuret of iron by exposure to air and moisture, being dried and exposed to a strong heat in earthen retorts. The acid of the salt is expelled, and condensed in receivers connected with the retorts; the first portion being weak, from the water still remaining in the salt being expelled with the acid. The product is more concentrated, as the process goes on, and towards the end the matter is even frequently obtained concrete, forming a substance known to the chemists by the name of Glacial Oil of Vitriol. It derives its concrete form, however, not merely from its state of concentration, but from the presence of a portion of sulphurous acid; it emits fumes, by exposure to the air; absorbs oxygen with a portion of humidity, so as to be converted into sulphuric acid, and may be formed directly, as Vauquelin found, by saturating sulphuric with sulphurous acid.

Besides this process, which is not now followed in this country, the chemists often attempted to obtain sulphuric acid by the combustion of sulphur. The attempt, however, could scarcely be said to be successful, the greater part of the product of the combustion of sulphur in atmospheric air being sulphurous acid, which is not easily condensed, or brought to the state of sulphuric acid. The process, however, was gradually improved, principally by adding to the sulphur a little nitre, and burning the mixture, and condensing the product, not in glass, but in vessels of lead.

This process, first established by Dr Roebuck *, to whose chemical knowledge, and public spirit, this country is so deeply indebted, and now so successfully conducted on a large scale, consists in mixing sulphur, in powder, with from one-eighth to one-tenth its weight of nitrate of potassa. A quantity of this mixture being put within a large leaden chamber, is kindled, the door of the chamber being closed. The sulphur, from the oxygen afforded partly by the atmospheric air, and partly by the nitrate of potassa, continues to burn, and from the oxygen being presented to it in this condensed state, combines with that proportion which forms principally sulphuric acid. A portion of nitric oxide gas, too, as Clement and Desormes have conjectured, may be volatilized, and may serve to convert part of the sulphurous acid which is likewise formed, into sulphuric acid †; a view of the subject which has been adopted by Gay Lussac. This acid, as well as a portion of sulphurous acid, are absorbed by water placed in the bottom of the chamber. At the end of

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* Edinburgh Philosophical Transactions, vol. iv. p. 69.

† Nicholson's Journal, vol. xvii. p. 41.

a few weeks this is highly acid; it is drawn off, and is concentrated, first by heating it in leaden vessels, and afterwards by boiling it strongly in glass retorts. The acid is at the same time purified; the sulphurous acid receives oxygen, probably from a portion of nitric oxide which is present; this oxide is decomposed or expelled; the acid, from being of a brownish colour, becomes colourless; it acquires an oily consistence, and a specific gravity of about 1.845.

Though the acid, prepared in this way, answers sufficiently well for the purposes to which it is applied in the arts, it cannot be regarded as perfectly pure. It always contains a little sulphate of potassa, formed from a portion of the potassa of the nitre having been dissolved by the sulphuric acid. The presence of this is rendered evident by diluting it with water; after the heat produced by the combination is diminished, the fluid is always more or less cloudy, and, on standing, deposites a precipitate, consisting principally of sulphate of potassa. There is reason to believe, that it consists in part, too, of sulphate of lead, derived from the vessel in which it has been prepared; at least Meyer has affirmed, that, in diluting 22 ounces of the concentrated acid, with an equal weight of distilled water, 6½ grains of a white powder were obtained, which, fused with borax, gave three grains of lead *; though, from some circumstances or other, the quantity has, in this experiment, been undoubtedly exaggerated. By dilution with water, the acid is in a great measure purified from these foreign substances, and it can be again concentrated,

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* Annales de Chimie, tom. vi. p. 30.

by exposing it to a strong heat in a glass retort. To render it perfectly pure for delicate chemical investigations, it is necessary that it should be distilled, a process, however, difficult from the high heat that is necessary, and which can be properly performed only on a small quantity of the acid.

Sulphuric acid is also formed, by combining sulphur with oxygen in other modes, as, for example, by distilling nitric acid from it. On applying heat to one part of sulphur, with eight or ten parts of nitric acid, in a retort, a large quantity of nitric oxide gas, mixed with nitric acid, forming dense orange fumes, is disengaged, and by pushing the heat sufficiently far, sulphuric acid, retaining a portion generally of sulphurous acid, is the residuum. This process, as is immediately to be observed, affords the best method of determining synthetically the composition of the acid.

It has been found difficult to determine the proportions of the constituent principles of this acid, owing partly to a portion of sulphurous acid being formed with it, in any experiment in which the direct combination of its constituent parts is effected, and partly to the difficulties attending all the modes of estimating the quantity of real acid produced.

Lavoisier, from some experiments on its direct formation, estimated the proportions of it at about 69 of sulphur, and 31 of oxygen.

Berthollet afterwards endeavoured to determine them from the quantity of sulphuric acid produced, either from the oxygenation of a certain quantity of sulphur, by heating it with nitre, or by distilling from it nitrous acid,—the quantity of sulphuric acid being estimated by combining it with potassa, or barytes, and ascertaining the quantity of the neutral salt that was formed. As the average result of these experiments, he fixed the proportions in real sulphuric acid at 72 of sulphur, and 28 of oxygen *. But as the quantity of sulphuric acid formed in these experiments was estimated from the proportions of the neutral salts given by Bergman, which there can be no doubt are not correct, the proportions of its elements, founded on that estimate, cannot be just.

Mr Chenevix, in a series of experiments on the analysis of some metallic sulphurets, in which part of the sulphur was converted by the agency of nitric acid into sulphuric acid, accordingly obtained results inconsistent with the proportions of that acid which had been assigned; and this led him to the farther investigation of the subject. He employed nearly the same method as that which formed the second experiment of Berthollet,—converting a given weight of sulphur into sulphuric acid, by distilling nitric acid from it repeatedly, (which he found might be done completely, and without any production of sulphurous acid), and determining the quantity of real sulphuric acid produced, by adding to the liquor a solution of nitrate of barytes, and weighing the quantity of sulphate of barytes thus formed. The quantity amounted to 694 parts, where 100 parts of sulphur had been employed, which is in the proportion of 100 parts from 14.5 of sulphur. By farther experiments, he sought to determine the proportion of sulphuric acid in sulphate of barytes, which he fixed

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[*] Mémoires de l'Acad. des Sciences, 1782, p. 602.

at 23.5 in 100 parts. Now, by the preceding experiments, these 23.5 parts contain 14.5 of sulphur; and this gives the proportions of 61.5 sulphur, and 38.5 oxygen in 100 parts sulphuric acid *.

In a report by Guyton, on a memoir of Thenard, on the oxides of antimony †, it is stated, that in his researches, he had determined, apparently by a method similar to the preceding, that sulphuric acid consists of 55.56 sulphur, and 44.44 oxygen.

The same investigation has occupied the attention of other chemists, and the results are still extremely various. In a short memoir on this subject, (*Annales de Chimie*, t. lviii. p. 122.), an abstract is given of some experiments by Klaproth, and of the results of the labours of some other chemists. Klaproth's experiments were made by converting sulphur into sulphuric acid, by the agency of nitric acid, and ascertaining the quantity formed by the quantity of sulphate of barytes obtained, by adding to it muriate of barytes; and the others appear to have been made by the same means. The proportions of the elements of real sulphuric acid are stated, according to

Klaproth, -	42.03 sulphur,	57.07 oxygen.
Richter, -	42.05 ———	57.95 ———
Bucholz, -	42.50 ———	57.50 ———
Trommsdorf,	70.00 ———	30.00 ———
Berthollet, -	72.00 ———	28.00 ———
Thenard, -	55.56 ———	44.44 ———
Chenevix, -	61.50 ———	38.50 ———

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* Transactions of the Irish Academy, vol. viii.; or Nicholson's Journal, vol. v. p. 126.

† Annales de Chimie, t. xxxii. p. 265.

These discordant results arise almost entirely from the mode of determining the quantity of sulphuric acid formed, by combining it with barytes, and calculating from the proportions of the elements of sulphate of barytes, which are by no means accurately fixed. Thenard proceeds on the supposition, that it consists of 74.82 barytes, and 25.18 of acid; Mr Chenevix, on the assumption that the proportions are 76.5, and 23.5; and as in the former, the sulphate is supposed to be calcined, these proportions nearly agree. Richter assumes that they are 69, and 31; and Klaproth takes the proportions given by Kirwan, of 67 and 33, with which those assumed by Bucholz correspond. It is scarcely possible to decide between these discordant results, which shew the errors the method is liable to, and prove the necessity of endeavouring to determine the proportions of the elements of sulphuric acid by some other mode. Those given by Mr Chenevix are not far from the mean of the others, and from this, as well as from there being reason to believe, that his estimate of the composition of sulphate of barytes, confirmed as it is by that by Thenard, is more accurate than the others, they are perhaps to be preferred.

The preceding are the proportions of real sulphuric acid; but in any state in which we can obtain it, a portion of water is always combined with it, and the precise quantity of this in an acid of given strength is not easily determined. This subject, of course, engaged the attention of Mr Kirwan, in his researches on the strength of the mineral acids; and he has given an extensive table of the proportions of real acid, in acids of different specific gravities. His method of finding the real acid, was to take an acid of a certain specific gravity, saturate a given weight of it with a certain base, with potassa for example, ascertain what quantity of base had been requisite for that purpose, and what quantity of the compound salt was formed. This, supposing the salt to be free from water, or if not, that the quantity it contains is ascertained, gave the quantity of real acid that had entered into the combination, and of course the quantity which had been contained in the acid, of the certain specific gravity which he had employed. He supposed, that the acid existing in sulphate of potassa is the real acid, or is combined with no water, as this salt loses no weight when exposed to nearly a red heat; and by the preceding method, he found what quantity of this real acid exists in an acid of certain specific gravity. The following table presents the results:

In Sulphuric Acid of different Densities, at 60°.			
1st Column.		*2d Column.*	
100 Parts Sp. Gravity.	Real Acid.	100 Parts Sp. Gravity.	Real Acid.
2,0000	89,29	1,4666	44,64
1,9859	88,39	1,4427	43,75
1,9719	87,50	1,4189	42,86
1,9579	86,61	1,4099	41,96+
1,9439	85,71	1,4010	41,07
1,9299	84,82	1,3875	40,18
1,9168	83,93	1,3768	39,28
1,9041	83,04+	1,3663	38,39
1,8914	82,14	1,3586	37,50
1,8787	81,25	1,3473	36,60
1,8660	80,36	1,3360	35,71
1,8542	79,46	1,3254	34,82

1st Column continued.		*2d Column continued.*	
100 Parts Sp. Gravity.	Real Acid.	100 Parts Sp. Gravity.	Real Acid.
1,8424	78,57	1,3149	33,95
1,8306	77,68	1,3102	33,03
1,8188	76,79+	1,3056	32,14
1,8070	75,89	1,2951	31,25
1,7959	75,—	1,2847	30,35
1,7849	74,11	1,2757	29,46
1,7738	73,22	1,2668	28,57
1,7629	72,32	1,2589	27,68+
1,7519	71,43	1,2510	26,78
1,7416	70,54+	1,2415	25,89
1,7312	69,64	1,2320	25,—
1,7208	68,75	1,2210	24,10
1,7104	67,86	1,2101	23,21
1,7000	66,96	1,2009	22,32
1,6899	66,07	1,1918	21,43+
1,6800	65,18	1,1836	20,53
1,6701	64,28	1,1746	19,64
1,6602	63,39	1,1678	18,75
1,6503	62,50	1,1614	17,85
1,6407	61,61	1,1531	16,96
1,6312	60,71	1,1398	16,07
1,6217	59,82	1,1309	15,18+
1,6122	58,93	1,1208	14,28
1,6027	58,03	1,1129	13,39
1,5932	57,14	1,1011	12,50
1,5840	56,25	1,0955	11,60
1,5748	55,36+	1,0896	10,71
1,5656	54,46	1,0833	9,80
1,5564	53,57	1,0780	8,93+
1,5473	52,68	1,0725	8,03
1,5385	51,78	1,0666	7,14
1,5292	50,89	1,0610	6,25
1,5202	50,00	1,0555	5,35
1,5112	49,11+	1,0492	4,46
1,5022	48,21	1,0450	3,57
1,4933	47,32	1,0396	2,67
1,4844	46,43	1,0343	1,78
1,4755	45,53		

Though sulphuric acid has been said to have been obtained so highly concentrated, as to have the specific gravity 2000, it is doubtful if it ever has, at least in a pure state, or unmixed with matter which might add to its specific gravity. Mr Kirwan, though he supposes that it may have been prepared of that strength in cold climates, was unable by any process to procure it. Dr Percival exposed to heat in a retort, until the bottom of the retort and the liquor itself appeared red,—a quantity of the common sulphuric acid of commerce, having the specific gravity 1.842; the specific gravity of what remained, and which amounted to about one third of the quantity originally employed, was 1.852, beyond which the concentration could not be carried, as what passed over towards the end of the distillation was as strong as what remained. Nor was it perfectly pure, as it let fall a quantity of a white powder when diluted with water. The acid which had distilled over, bore dilution without having its transparency impaired; it could not be concentrated farther than the specific gravity 1.846.

Sulphuric acid has, however, been obtained concrete or crystallized. It is obtained in this state, as I have already remarked, in the distillation of it from the dried sulphate of iron, forming the Glacial Oil of Vitriol of the older chemists. There can be no doubt, however, that it owes this form, not to its mere state of concentration, but to the presence of sulphurous acid. This acid, added to pure sulphuric acid, renders it capable of congealing at a comparatively moderate temperature, and the concrete acid from the sulphate of iron gives fumes of sulphurous acid, and when deprived of this acid it becomes liquid.

Sulphuric acid, in the state in which it is usually met with in commerce, has a specific gravity not exceeding 1845, containing, when of this strength, according to Mr Kirwan's table, 79 of real acid, and 21 of water. It is of an oily consistence and appearance, perfectly inodorous, colourless and transparent, but very liable to acquire a brown tinge from the smallest quantity of carbonaceous matter. It possesses in an eminent degree all the properties of an acid; so much so indeed, that it has been usually considered as the most powerful of the class. Even when diluted with 20 or 30 parts of water, its taste is extremely sour, and it reddens instantly the vegetable colours. It is highly corrosive, so as immediately to erode any animal or vegetable matter.

Sulphuric acid is capable of congealing by cold, undergoing even a regular crystallization. Its freezing point is very different, according to its state of concentration, and on this subject there are some rather singular facts. The Duke D'Ayen had observed that the concentrated acid congealed when exposed to a cold of —13° Reaumur, but that when mixed with two or more parts of water, it could not be frozen, at least unless very much diluted, when a portion of the water probably was congealed. These experiments were confirmed by Guyton, who observed, too, that the concentrated acid, when congealed, remained in that state at a much less cold than that necessary to freeze it. Mr Macnab, in his experiments at Hudson's Bay, found that sulphuric acid of the specific gravity 1843, congealed at —15° of Fahrenheit, while the same acid, diluted with rather more than half its weight of water, required to congeal it a cold of —36°, and, when still further diluted, required still more intense colds. In these experiments, only a portion of the acid congealed; but on separating the liquid part from this, both were found of nearly the same strength. The subject was afterwards investigated by Mr Keir [*], who found that there is a certain point of strength of the acid, at which it congeals most readily, and that a very small variation above or below this renders it incapable of freezing without a considerable augmentation of cold. This strength is when the acid is of the specific gravity of 1780; this liquid, as well as in the intermediate states of dilution, from this to 1786 on the one hand, or 1775 on the other, freezes when exposed to the cold of melting snow; and when more diluted or more concentrated, the freezing became proportionally more difficult, or required a higher temperature. Mr Keir observed, too, the singular fact taken notice of by Guyton, that the acid remained congealed at a higher temperature than that necessary to congeal it. The above diluted acid, for example, could not be congealed by a temperature above 32°; but when congealed by surrounding it with melting snow, it remained solid at higher temperatures, and when it began to melt, a thermometer immersed in it indicated 45° of Fahrenheit; or if cooled, as it might be by avoiding agitation, to 29°, on agitating it, it instantly congealed, and the temperature rose to 46°. The figure of the crystals, as described by Mr Keir, is that of a six-sided prism, bevelled at both extremities; by Chaptal [†], a six-sided prism, acuminated by six planes:

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[*] Philosophical Transactions, vol. lxxvii. p. 267.

[†] Mémoires de l'Acad. des Sciences, 1784, p. 624.

the crystals are often large and hard; they are more heavy than the part which remains liquid. Mr Keir also observed, that the congealed portion contained a number of air bubbles: And, were the experiments of Ritter on the decomposition of water by freezing confirmed, these facts might lead to the supposition that some such decomposition happened in the congelation of sulphuric acid.

Sulphuric acid boils, according to Bergman, at 540°; according to Dalton at 590°; and condenses unchanged. By a very high temperature, as by passing it through an ignited tube, it is decomposed and resolved into oxygen and sulphurous acid gases *.

The attraction of this acid to water is extremely strong; it is always found combined with it, and cannot by any process be entirely separated from it. When exposed to the atmosphere, it attracts rapidly the portion of watery vapour that is present, so as soon to increase sensibly in weight. In the course of a month, if it has been freely exposed, its weight will be more than doubled; the farther absorption becomes then more slow, until the equilibrium is arrived at, between the attraction of the acid, and the tendency of the water to pass into the elastic form. When the concentrated acid and water are directly mixed together, they combine in every proportion without interruption, an increase of density and a production of heat attending the combination. The increased density, or the deviation from the mean density of the water and acid, is greater as the acid is in larger proportion to the water. The production of heat is also greater. From mixing two

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* Mémoires de la Société d'Arcueil, t. i. p. 242.

parts of concentrated acid with one part of water, Gadolin found the elevation of temperature equal to 203 degrees of Fahrenheit; equal parts produced a rise equal to 175°, and from one part of acid with two of water the rise was 108°. Lavoisier and La Place, by making this combination in the calorimeter, found that from the mixture of 2 lbs. of sulphuric acid with 1½ lb. of water, as much caloric was extricated as melted above 3 lbs. of ice, that is, as much ice as would have been melted by 2 lbs. 6 ounces of boiling water. This increase of temperature is owing to a diminution of capacity, as was experimentally proved by Gadolin. When the acid is added to ice or snow, it melts it rapidly; and from the absorption of caloric by the liquefaction of the ice, there is a considerable reduction of temperature; this, however, is counteracted to a certain extent by the heat arising from the condensation, and hence the cold is greater, as has been already observed, (vol. i. p. 469), when the acid is previously diluted with a portion of water.

By combination with water, the properties of the acid are merely weakened, not materially changed.

Sulphuric acid does not appear to form any combination with the simple gases. Giobert had stated some experiments, particularly that of distilling it from black oxide of manganese, to prove that a combination of it with oxygen exists, forming an oxy-sulphuric acid; but these have been found inaccurate or inconclusive by Vauquelin and Chenevix. Hydrogen gas appears, from the experiments of Priestley, to be capable of decomposing it at a high temperature, a portion of sulphur being produced by exposing sulphuric acid inclosed in a vessel with hydrogen gas to the solar light, concentrated by a lens.

Sulphuric acid absorbs nitric oxide gas, and acquires, according to Dr Priestley's observation, a purple colour from this impregnation. It unites also with nitric acid, and Mr Keir observed a singular property of this compound, that it dissolves silver, without dissolving copper, or almost any other metal. He proposed an acid of this kind, prepared by dissolving 1 lb. of nitre in 8 or 10 lbs. of sulphuric acid, as a cheap solvent, for separating silver from plated copper *.

The primary inflammables decompose sulphuric acid. When exposed to heat with charcoal, its oxygen is partially abstracted, and a large quantity of sulphurous acid gas and carbonic acid gas rapidly discharged. If mixed with any vegetable or animal matter, it acquires a brown colour, a change which is apparently owing to the hydrogen of the vegetable matter attracting partially the oxygen of the acid, and to a portion of charcoal being evolved; hence, if heat be applied to an acid coloured, from this cause, the colour is at length discharged, the charcoal being fully oxygenated or converted into carbonic acid, which is expelled. The addition of a little nitrous acid has the same effect, obviously by the same agency. If the vegetable substance be one containing much hydrogen; as, for example, if one of the fixed, or more especially of the volatile oils, be added o the acid, the mutual action becomes rapid even in the cold; the mixture becomes black; the temperature rises, sometimes even so high that the oil is inflamed, and sulphurous acid and carbonic acid gases are extricated. If the proportion of car-

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* Philosophical Transactions, vol. lxxx. p. 360.

bonaceous matter be small, so as to admit of the application of a moderate heat with safety, the abstraction of oxygen from the acid is even complete. This was long ago observed by Boyle, who obtained a portion of sulphur from the distillation of sulphuric acid and oil of turpentine.

Sulphur boiled with sulphuric acid receives from it a portion of oxygen; andif a due proportion be observed, the whole may be converted into sulphurous acid. Phosphorus, with the aid of a high temperature, produces in it a similar decomposition.

Sulphuric acid is likewise decomposed by the greater number of the metals, at least at a high temperature; they attract its oxygen partially, and disengage sulphurous acid, the metallic oxide combining with the remaining acid. If diluted with from 4 to 7 parts of water, the nature of the action it exerts is different; the metal does not decompose the acid but the water, attracting its oxygen, and of course disengaging the hydrogen, which passes to the elastic state; the metallic oxide combines with the acid, and from the portion of water present, remains in solution. This solution proceeds rapidly even in the cold, but is confined to those few metals which shew a strong attraction to hydrogen, principally to iron and zinc; copper is affected in a similar manner, though more slowly. The nature of this action has been already explained, (vol. i. p. 100).

Sulphuric acid combines with the alkalis, earths, and metallic oxides, and in a certain proportion the result is a mutual neutralization of properties. It has been supposed to have a stronger attraction to them than the other acids have, as its salts are decomposed with more difficulty than the others, while on the other hand it decomposes, at least when aided by a high temperature, a number of the other neutral salts, disengaging their acid; but this is owing, not so much to the predominant strength of affinity, as to its greater comparative fixity. In the humid way, the decompositions it produces, like those of the other acids, are generally partial, and influenced by proportion, cohesion, and other external forces. Barytes forming with this acid a very insoluble compound, all its salts give a copious precipitate with barytic water, or muriate or nitrate of barytes, a test by which they are recognised. The Sulphates, as the neutral salts formed by this acid are named, are decomposed by exposing them to heat, mixed with carbonaceous matter, a portion of sulphur remaining in combination with the base, and by this chemical character they are particularly distinguished. They are in part also decomposed by heat alone. On the results of this decomposition, a series of experiments has lately been made, by Gay Lussac *. He has drawn from them the following conclusions. All the metallic sulphates are decomposed by heat, giving results which depend on the affinity of the base to the acid. Those in which the acid is little condensed, give, by distillation, sulphuric acid: those in which it is retained more strongly, and which are insoluble, give sulphurous acid and oxygen. Those which form a medium between these, and which are acidulous and soluble, give sulphuric acid, sulphurous acid and oxygen. All the earthy sulphates, which have an excess of acid, are decomposed by heat, giving sulphuric acid, oxy-

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* Mémoires de la Société d'Arcueil, t. i. p. 215.

gen gas, and sulphurous acid. The neutral alkaline sulphates are not decomposed by heat, with the exception of sulphate of ammonia; but when they are crystallized with an excess of acid, part of that excess is by heat converted into sulphurous acid and oxygen. These decompositions require a high temperature; and at a lower temperature the reverse combinations, Gay Lussac has shewn, are established. Thus, if a metallic sulphuret, or even an earthy or alkaline sulphuret, be roasted with a low red heat, the air being admitted, sulphuric acid is formed, and of course a sulphate is produced; but by raising the temperature higher, this sulphate is decomposed,—a fact of importance in practical chemistry, both as relating to the preparation of certain sulphates on a large scale, and to the roasting of metallic ores.

SULPHATE OF POTASSA.—This salt, long known to chemists under various appellations, is easily formed by adding diluted sulphuric acid to a dilute solution of potassa, or, what is more economical, of carbonate of potassa, until the acid and alkaline properties are mutually neutralized. A cheaper process, and which is generally followed in pharmacy, (the principal consumption of this salt being for medicinal purposes), is to prepare it from the residual mass obtained in the distillation of nitric acid from nitre and sulphuric acid. This is sulphate of potassa with an excess of acid. It is dissolved in water; a solution of carbonate of potassa is added until the excess of acid be saturated; the liquor is strained, and by evaporation affords the neutral sulphate of potassa.

It crystallizes by slow evaporation, its crystals being small and grouped; their figure is that of a six-sided prism, acuminated by six planes, subject, however, to various modifications. It is not deliquescent, and scarcely efflorescent; it decrepitates when heated, and by a heat sufficiently strong is melted into a kind of glass. 17 parts of water, at the temperature of 60°, are requisite for its solution; at 212°, 5 parts are sufficient. Its taste is bitter.

Like the other sulphates, it is decomposed by exposing it to the heat of ignition in mixture with charcoal, or any carbonaceous matter, the oxygen of its acid being abstracted, and the sulphur remaining united with the alkali, forming a compound which may be abstracted from the residual charcoal by solution in water. If iron be mixed with the salt and the charcoal, it attracts much of the sulphur, and allows the alkali to be obtained with less loss; and this process has been proposed as a method of extracting the alkaline base of this salt. Lime has a similar effect with iron, the salt being decomposed, and the alkali obtained by exposing the sulphate to a red heat mixed with charcoal and carbonate of lime *.

A decomposition of this salt, which much engaged the attention of chemists, from being regarded as anomalous, is that which it suffers from nitric or muriatic acid. If it be digested with a portion of nitric acid with a very moderate heat, a portion of nitrate of potassa is found to be formed; a proof that the sulphate has been at least partially decomposed, and a proportion of its base combined with the nitric acid. Yet we know that sulphuric acid decomposes nitrate of potassa, and hence the results

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* Journal de l'Ecole Polytechnique, Cah. ii. p. 185.

appear contradictory; the nitric acid in the one experiment apparently exerting a stronger attraction to the potassa than the sulphuric acid; and in the other, the reverse appearing to be the case. I have already stated the explanation which Bergman gave of this anomaly, founded on the hypothesis that sulphate of potassa has an attraction to an excess of sulphuric acid, and that the decomposition (which is always partial) is owing partly to this, and partly to the affinity of sulphuric acid to potassa; and have likewise observed, that the whole is an example of the participation of a substance between the other two, which have affinities towards it, and that it affords an excellent illustration of the effect of proportion on the results of chemical attraction. Notes, vol. i. p. 596.

This salt, according to Mr Kirwan's table, consists of 54.8 of base, and 45.2 of acid. If his assumptions be just, it affords an example of a salt having no water of crystallization.

Sulphate of potassa is not applied to any important use. It is sometimes employed in medicine. From the alkali it contains, it is used in the manufacture of alum, potassa entering into the composition of that salt; and it is employed in some metallurgic operations as a flux. For the two latter purposes, the residuum of the distillation of nitric acid, which is sulphate of potassa with an excess of acid, is used. It is known to the artists by the old name of Sal Enixum.

Potassa easily combines with sulphuric acid in other proportions, besides that which gives rise to mutual neutralization. When combined even with a considerable excess of acid, which may be done by exposing it to heat in a glass vessel, with one-third its weight of the acid, it is capable of becoming solid, forming a mass of a crystalline texture; or if its solution has been slowly evaporated, distinct crystals of a prismatic form. This supersulphate has a sour taste, and reddens the vegetable colours; it is much more fusible, and more soluble than the neutral sulphate in water, and is not deliquescent; by repeated solutions and crystallizations, a great part of the excess of acid is removed from it. Part of the acid, though perhaps not the whole of it, may also be driven off by a strong heat, partially decomposed.

Sulphate of Soda.—Glauber, a German Chemist, or rather alchemist, examining the residuum in the distillation of muriatic acid from muriate of soda and sulphuric acid, discovered this salt, which from him derived the name by which it is commonly known. It was introduced, and largely employed in medical practice; and hence it has been prepared by various processes on a large scale. One source of it is that pointed out by Glauber,—the distillation of muriatic acid; the saline mass which forms the residuum consists of the soda of the muriate of soda, with sulphuric acid in excess. It is dissolved in water; the excess of acid is neutralized by adding a sufficient quantity of lime; the fluid is allowed to remain until it becomes clear; it is drawn off into shallow leaden vessels, and on cooling affords the neutral sulphate in crystals. It is also obtained in large quantity in the manufacture of sal ammoniac, or muriate of ammonia. By various processes a sulphate of ammonia is procured, which is mixed with muriate of soda; the mixture being exposed to a strong heat, the muriatic acid and the ammonia combine, and form a salt, which is at the same time sublimed. The residual mass is consequently sulphate of soda; it is dissolved in water; a portion of lime is added, to disengage any small portion of ammonia that may remain; and the sulphate of soda is crystallized, as in the preceding method. This salt also exists native in mineral springs. It sometimes effloresces on the walls of old buildings.

Sulphate of soda crystallizes in six-sided prisms, bevelled at the extremities, and longitudinally grooved. Its taste is strongly saline and bitter. It is efflorescent; exposed to a dry atmosphere the surface of the crystals soon becomes white and opaque, and at length they fall into powder. It is soluble in rather less than three times its weight of water at 60°; and in less than its own weight at 212°. Exposed to heat it undergoes the watery fusion; the water of crystallization is soon dissipated; and by urging it with a strong red heat it may be melted.

Sulphate of soda suffers decompositions similar to those of sulphate of potassa. Barytes and strontites abstract its acid completely; potassa partially; nitric and muriatic acids digested upon it, share its base with the sulphuric acid. Heated with carbonaceous matter, its acid is decomposed; and this process is sometimes followed in the arts to procure soda, lime or iron being added to combine with the sulphur of the acid.

According to Kirwan, crystallized sulphate of soda consists of 18.48 of soda, 23.52 of acid, and 58 of water. When its water of crystallization is expelled by a heat of 700°, it consists of 44 of soda and 56 of acid.

Sulphate of Ammonia.—This salt is one of little importance. It crystallizes in six-sided prisms acuminated by six planes, the crystals being generally slender. It is soluble in about two parts of water at 60°, and in an equal weight of boiling water. It is slightly efflorescent. Exposed to heat, it melts, and is decomposed, part of the ammonia being exhaled. At ignition, it suffers a different decomposition, from the re-action of the elements of its immediate constituent principles, the hydrogen of the ammonia attracting part of the oxygen of the acid, and sulphurous acid and nitrogen being disengaged in the elastic form. It deflagrates gently when heated with nitre.

Sulphate of ammonia, like the two preceding salts, is partially decomposed by nitric and muriatic acids. The other two alkalis, lime, barytes and strontites, attract its acid, and with the assistance of heat displace the ammonia. According to Kirwan it consists of 54.66 of acid, 14.24 of ammonia, and 31.1 of water. It is applied to no use. It has been said to have been found in the neighbourhood of volcanoes. The saline matter extracted from soot by maceration in water consists partly of it, and is employed in the preparation of muriate of ammonia.

Sulphate of Barytes.—This salt is formed whenever barytes is presented to sulphuric acid, even although either the earth or the acid be in any previous state of combination. Though it exists in nature in a crystallized form, it can be obtained artificially only in the state of a powder. It is insoluble in water, or at least cannot be dissolved in any appreciable quantity. It is perfectly tasteless. The specific gravity of the native sulphate is 4.4. It is fused by a very strong heat: a small fragment of it is melted by the blowpipe into an opaque globule. When heated with carbonaceous matter, its acid is decomposed, and a sulphuret of barytes is formed. It is partially decomposed when heated with some of the other neutral salts, as, for example, with carbonate of potassa or of soda; more sparingly, with muriate of soda; and almost completely, with muriate of lime when the two salts are mixed in equal proportions: this, according to Trommsdorff and Goëtling, affords an easy mode of obtaining muriate of barytes *. With regard to the composition of sulphate of barytes, the statements, by different chemists, present very discordant results, though the determination of it is of importance, as it often forms the basis of the estimation of the quantities of sulphuric acid in compounds, decomposed by the agency of barytes. According to Fourcroy, the artificial sulphate consists of barytes 64, sulphuric acid 33, and water 3. According to Kirwan, when it is ignited, it is composed of 78 barytes, and 22 of acid; and this also he states as the composition of the natural sulphate. Bergman had given as the proportions, 84 of barytes, 13 of acid, and 3 of water. By Withering, they were stated to be 67.2 of earth, and 32.8 of acid; with which the analysis by Klaproth almost exactly agrees. Thenard, in his investigation of the composition of sulphuric acid, states them at 74.8 and 25.2, the sulphate being calcined †: and Mr Chenevix at 76.5, with 23.5 of acid ‡. It is difficult to determine which of these proportions is just.

Barytes can combine with an excess of sulphuric acid, and forms a liquid that congeals into a congeries of prisms; it is decomposed, and the neutral sulphate precipitated, on the affusion of water.

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* Nicholson's Journal, vol. xi. p. 133.

† Annales de Chimie, tom. xxxii. p. 266.

‡ Nicholson's Journal, 4to, vol. v. p. 347.

Sulphate of Strontites is in the form of a white powder, insipid, and apparently nearly insoluble in water; requiring at least, according to Dr Hope, nearly 4000 parts for its solution. It combines with an excess of acid, and is thus rendered soluble in water, and crystallizable. It exists native, and in this state appears to be composed of 58 of earth and 42 of acid; or, according to Vauquelin, of 54 of earth and 46 of acid.

Sulphate of Lime has been long known to chemists under the names of Gypsum and Selenite, and is one of the saline substances most abundant in nature. It forms immense strata, composing entire mountains: it is to be found in greater or less quantity in almost every soil: it is contained in the waters of the ocean, and in almost all river and spring water. Its presence in these is the cause of the quality termed hardness, which, independent of the peculiar taste by which it is accompanied, is known by the water being incapable of forming a solution of soap; the sulphuric acid of the sulphate of lime attracting the alkali of the soap, and the oil forming an imperfect saponaceous compound with the lime.

Sulphate of lime is insipid: it is white, and soft to the touch. It requires not less than 500 times its weight of water for its solution at a mean temperature. At that of 212 it is considerably more soluble, and this latter solution, upon cooling slowly, deposites minute crystals. It is found native regularly crystallized.

Exposed to heat it appears to effervesce or boil, an appearance owing to the expulsion of its water. It becomes opaque, and falls into a white powder. This is what is termed Plaster, and is used in the formation of what is named Stucco work. When water is poured on it, it absorbs it rapidly; and though as much water be added as forms a liquor of the consistence of thick cream, it soon becomes hard; hence it is easily cast into moulds, and is used for statuary. This hardness is acquired probably in consequence of a hasty crystallization: it is promoted by the addition of a little calcined lime.

When exposed to a more intense heat, it seems to vitrify, but this is owing to the action of some other earth mixed with it, or derived from the crucible, since when placed on a piece of pure chalk, it is infusible even by the strongest concentrated solar light. By heating it on charcoal, or by the blowpipe, it is partially decomposed, part of the oxygen of its acid being abstracted: and when exposed to the heat excited by a stream of oxygen, it is, after this partial decomposition, completely vitrified.

This salt is decomposed by barytes and the fixed alkalis, when boiled with them in water. It is decomposed also by double affinity, by boiling it in a solution of the alkaline carbonates. It is not decomposed by any of the acids. It may be dissolved by the sulphuric, but the solution is decomposed by water. The proportions of its constituent parts are, according to Kirwan, when dried at 66°, 32 of lime, 46 of acid, and 22 of water: when it has been kept ignited, 41 of lime, and 59 of acid.

The principal use of this substance is in statuary. From the property it acquires, by calcination, of hardening, when mixed with water, it can be applied to the construction of various ornaments, which are sufficiently durable if not exposed to moisture.

Sulphate of Magnesia. This salt is found in sea-water, and in many mineral waters. The mineral springs of Epsom once afforded a large part of what was used in commerce; and hence it was commonly known by the name of Epsom or English salt. At present it is chiefly extracted from sea-water, in which it is contained with a portion of muriate of magnesia. These salts remain dissolved in the liquor which remains after the crystallization of the sea-salt. This brine, or Bittern as it is termed, is either boiled down until it afford the sulphate of magnesia, on cooling, in acicular crystals; or sulphate of iron is added, the sulphuric acid of which combines with the magnesia of the muriate of magnesia, and thus increases the quantity of sulphate that is obtained.

This salt, as it is usually met with, exhibits a confused mass of needle-like crystals, which are deliquescent. The deliquescence is owing to the admixture of muriate of magnesia, as the pure sulphate is rather efflorescent. By slow or spontaneous evaporation of its solution, it crystallizes in the form of quadrangular prisms acuminated by four planes. These crystals effloresce on exposure to the air: they are soluble in little more than their own weight of water, at the temperature of 60°, and in three-fourths of their weight of boiling water. They undergo the watery fusion at a very moderate temperature, and lose half their weight, from the expulsion of their water of crystallization. The dry mass which remains is melted in a strong heat, but is not decomposed. One hundred parts of crystallized sulphate of magnesia consist of 29.35 parts of acid, 17 of earth, and 53.65 of water. Its taste is very bitter, and the bitterness of sea-water and many mineral springs is owing in part to its presence.

Sulphate of Argil. Sulphuric acid combines with argil. The salt long known by the name of Alum was supposed to be formed from this combination, having only an excess of acid. It has been found, however, always to contain potassa, or ammonia, one or other of which is even essential to it; and hence it differs from the proper sulphate of argil.

When pure argil is dissolved in sulphuric acid, it is difficult to bring so much into solution as is sufficient to neutralize the properties of the acid; but, by boiling the solution with an additional portion of argillaceous earth, the neutral compound, or proper sulphate of argil, is obtained. It crystallizes in the form of thin scales, white, and of a pearly lustre, which alters little by exposure to the air: its taste is astringent: it is very soluble in water: when exposed to heat, its water of crystallization is dissipated, and, by a stronger heat, its acid is expelled. According to Bergman, it consists of 50 of argil, and 50 of sulphuric acid.

When argil is combined with an excess of sulphuric acid, the compound crystallizes with more difficulty, as, on evaporation, it assumes a gelatinous consistence. Small brilliant crystals, however, are formed in it.

Alum is a ternary compound of argil, potassa, and sulphuric acid; sometimes even a quaternary one, ammonia entering into the composition; and there being always an excess of sulphuric acid. It had been long known, that in the manufacture of alum, from what were named Alum Ores, it was often necessary to add a portion of alkali, either the potash of commerce, or an impure ammonia, to cause the salt to crystallize. The operation of this was supposed to be, the correcting the too great excess of acidity, which, it was imagined, prevented the crystallization, by adding to the solubility of the combination. Yet Bergman observed, what was subversive of this opinion, that soda or lime does not promote the crystallization; and he even found, that a portion of potassa exists in several of the varieties of alum of commerce, though he appears to have regarded it as accidental, not essential to their composition. This subject was more completely investigated about the same time by Vauquelin, and by Chaptal *, who proved, that the sulphate of argil, either neutral or acidulous, cannot be crystallized but with much difficulty, and in small plates; but that, on adding to the concentrated solution a few drops of a solution of potassa, the crystallization immediately commences, and, by adding the requisite quantity, the whole may be obtained in the state of crystallized alum. The same effect was obtained from the addition of sulphate of potassa.

The alum of commerce is generally a super-sulphate of argil and potassa. According to Vauquelin's mode of stating the results of his analysis, it consists of 49 of sulphate of argil, 7 of sulphate of potassa, and 44 of water. Thenard, in his analysis of the different kinds of alum met with in commerce, has stated the composition at sulphuric acid 26.04, argil 12.53, potash 10.02, water 51.41 †. Native crystallized alum was found by Klaproth to be composed of 15.25 of argil, 7.5 of oxide of iron, 0.25 of

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* Annales de Chimie, tom. xxii. p. 258. 280.

† Nicholson's Journal, vol. xviii. p. 282.

potassa, and 77 of acid and water of crystallization. Sometimes the alum of commerce contains ammonia, which has been added to it in its preparation, and which is discovered by its odour when lime is added to its solution. And it appears, that the triple salt of sulphuric acid, argil, and ammonia, is similar in its properties to alum, though it is not met with among the alums of commerce. In almost all the alums of commerce, too, a minute quantity of iron is present; this appears, from the experiments of Thenard, to have an injurious effect in dyeing on some of the more delicate colours, especially in silk dyeing, and to this freedom from iron is owing the preference that has been given to Roman alum.

Alum is often a natural product. It occurs efflorescent, in the layers of a species of slate often found in connection with coal, and which, from producing this salt, has received the name of Alum Slate. It appears, that in this fossil, sulphur is present, perhaps in the state of sulphuret of iron; that, from long exposure to the air, the sulphur is oxygenized, and converted into sulphuric acid, which re-acts on the argil, the basis of the slate, and combines with it. As the alum effloresces in regular crystals, potassa must also be present, and indeed, from Klaproth's analysis, is proved to be contained in the native alum. Vauquelin accordingly found, in one fossil of this kind which he analysed, the Alum Ore as it is named of La Tolfa, potassa, in the quantity of 3.4 *per cent.* Large quantities of alum are thus obtained in different countries.

In a large coal-mine near Glasgow, which has been wrought at least 200 years, the aluminous slate above the coal has been fully exposed, and the circumstances being favourable for the production of native alum, the formation has taken place to a great extent, and large quantities of alum are procured.

In circumstances which are not favourable for the natural oxygenizement of the sulphur in the alum slate, and the consequent formation of alum, an artificial process is followed. The alum ore, as it is named, is calcined with a low heat, by which the sulphur is more or less completely converted into sulphuric acid; the oxygenation is completed by exposing the calcined ore to the air, with the presence of humidity; an acidulous sulphate of argil is formed: this is extracted, by washing the materials with water. The solution seldom is capable of affording alum by evaporation, from the absence of the proportion of potassa requisite to the constitution of the salt: there is therefore added to it a solution of the potash of commerce, or, what is now more economically used, the acidulous sulphate of potassa, obtained in the distillation of nitric acid, or the muriate of potassa, contained in the residual liquor from the manufacture of soap; and, by evaporation of the ley, the alum is obtained by crystallization.

It appears from Klaproth's examination of some of the slates which afford native alum, that the product may be much increased, by adding a proportion of alkali to the liquid obtained by their lixiviation; the slate not containing so much alkali as is necessary to convert the whole sulphate of argil into alum.

Alum, as it is usually met with, is in large masses destitute of figure, but of a crystalline texture, transparent, and colourless. What is named Roch Alum in commerce is in smaller crystalline fragments, less transparent, and of a red tinge. When alum is regularly crystallized, the form of the crystals is an octaedron. It is soluble in 15 parts of cold, and in two parts of boiling water: its crystals are slightly efflorescent: its taste is sweetish and astringent. Its solution reddens the vegetable colours, from the excess of acid in the salt.

Alum melts when exposed to a very moderate heat, from the water of crystallization which it contains dissolving the solid salt. As this evaporates, it leaves the salt in the form of a light white powder, named Burnt or Calcined Alum. It is merely the alum deprived of its water of crystallization, with a very small portion of acid. It reddens the vegetable colours, and its taste is stronger than that of the crystallized salt. By a strong heat, the acid is partly expelled, partly decomposed, a quantity of oxygen being afforded by its decomposition.

This salt is decomposed by the three alkalis,—by barytes, lime, and magnesia, which attract the greater part of the acid, and precipitate the earth with a small quantity of acid combined with it.

A different kind of decomposition is that which it suffers from being exposed to heat with carbonaceous matter: the oxygen of its acid is partially abstracted, and a sulphite of argil remains. A decomposition of this kind, in which a large proportion of carbonaceous matter is used, affords a product which burns spontaneously on exposure to the air. This substance is named Pyrophorus: it is prepared by exposing to heat in an iron-pot, three parts of alum, with one part of flour: the mixture liquefies, and is to be stirred constantly till the whole becomes grey, and easily reducible to powder while hot. The coarse powder is put into a coated phial, so as nearly to fill it: the mouth of the phial is stopt with a small plug of clay, and is placed in a crucible, and surrounded with sand up to the neck. The crucible is heated to redness, until a blue flame appears at the mouth of the phial: when this has continued ten minutes, the crucible is removed from the fire, and the phial, when sufficiently cold, is accurately stopt.

This substance inflames in atmospheric air: in a moist atmosphere the inflammation is more speedy, and in a dry air it can scarcely take place. It burns brilliantly in oxygen gas, in nitrous gas, and oxymuriatic acid gas, and is inflamed by the sulphuric and nitric acids.

It has been proved, that in order to form Pyrophorus, the alum must contain potassa; and the following has been given as the theory of its preparation, and of its spontaneous inflammation: The carbon of the vegetable matter employed decomposes the sulphuric acid; and carbonic acid, with sulphurous acid, and sulphuretted hydrogen gases, are disengaged. The potassa of the alūm combines with a portion of sulphur, and forms a sulphuret, which is intimately diffused through the argillaceous earth. There likewise remains a considerable quantity of charcoal in the same intimate mixture, and all these substances are perfectly dry. When exposed to the air, moisture is rapidly absorbed by the sulphuret, by which the temperature is raised: at the same moment, the sulphur is enabled, by a disposing attraction exerted by the potassa, to absorb oxygen: it is inflamed, and thus kindles the dry carbonaceous matter; the inflammation of both being much facilitated by their extreme division, from their intimate mixture with the argillaceous earth, and the extensive surface they thus present to the air.

Alum is used in a variety of arts. It hardens tallow: it increases the adhesive power of the farinaceous pastes: it renders water clear, which is turbid from the admixture of earthy particles; and it is one of the most essential articles in the art of dyeing, fixing the colours, and often adding to their brilliancy. It is used in medicine as a powerful astringent.

If a solution of alum be boiled with a portion of argillaceous earth, its excess of acid is saturated, and it becomes insoluble: it is precipitated therefore in the state of a powder, which is insipid. From the experiments of Chaptal, it appears too, that an excess of potassa may enter into the composition of alum, so as to alter its properties: with a certain quantity, more than what is contained in common alum, the salt crystallizes in cubes, and, with still more, it falls down in flocculi.

The other sulphates have been little examined. SULPHATE OF ZIRCON is insipid and insoluble. SULPHATE OF GLUCINE is difficultly crystallizable; its taste is saccharine and astringent; it is very soluble in water, its solution assuming by concentration the consistence of a syrup: it is decomposed by heat. SULPHATE OF ITTRIA crystallizes in small brilliant grains, according to Klaproth of a rhomboidal form, and of a colour inclining to amethyst red. Their taste is sweet and astringent. They require from 25 to 30 parts of water for their solution, and are not more soluble in hot water. The sulphuric acid is expelled by a red heat.

The remaining combinations of sulphuric acid fall to be considered under the history of the substances to which they belong. The acid itself is of very extensive use. It is one of the most important agents in chemical investigations, either by the affinities it directly exerts, or by the oxygen it communicates. In the arts it is much used; as in bleaching; in some of the processes of dyeing; in some metallurgic operations; and in the preparation of a number of the neutral salts.

SECT. III.

OF SULPHUROUS ACID.

This acid had been known to the earlier modern chemists, and in some of its combinations had been examined by Stahl. Priestley shewed that it is a permanently elastic fluid. Berthollet pointed out its relation to sulphur and sulphuric acid *, and its history was completed in an elaborate memoir by Fourcroy and Vauquelin, from which principally the following account of it is taken †.

Sulphurous acid is obtained, as has been just remarked, by the slow combustion of sulphur, but it is mixed with a little sulphuric acid, and it is not easy to conduct the process so as to obtain it pure. Chemists procure it, therefore, rather by decomposing sulphuric acid by the action

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* Mémoires de l'Acad. des Sciences, 1782, p. 597.

† Annales de Chimie, tom. xxiv., or Nicholson's Journal, 4to, vol. i. p. 313.

of substances which are capable of partially abstracting its oxygen, and which do not form an aëriform product. The metals answer to this character; those should be employed which do not decompose water, as from the portion of water which even the concentrated sulphuric acid contains, a little hydrogen gas might be evolved. Quicksilver, or tin, on the whole, answers best. One part of either is put into a retort, with two parts of sulphuric acid; heat is applied by a lamp, the metal attracts part of the oxygen of the acid, and the sulphurous acid which is disengaged is received over mercury.

The composition of sulphurous acid is not easily determined, as to the proportions of its constituent parts. They have been stated at 85 sulphur and 15 oxygen. Dr Thomson, from a series of experiments on the compounds of sulphur and oxygen, states them at sulphur 68, oxygen 32 *.

This acid exists in the state of gas. It has however been reduced to the liquid state; this was effected by Monge, by the application of intense cold, and strong pressure. Mr Northmore, by pressure alone, succeeded in condensing it into a thick fluid of a dark yellow colour, which immediately evaporated on the removal of pressure †.

In its usual state the specific gravity of this gas is, according to Bergman, 0.00246, according to Lavoisier 0.00251, or it is more than twice as heavy as atmospheric air. It has a suffocating pungent odour, proves speedily fatal to life, and instantly extinguishes combustion.

It appears to be decomposed by heat, and resolved into

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* Nicholson's Journal, vol. vi. p. 97.

† Ibid. vol. xiii. p. 236.

sulphur and sulphuric acid. The production of sulphur was observed by Priestley, from exposing its aqueous solution to a high temperature in glass tubes hermetically sealed. Vauquelin also observed the deposition of sulphur, and the production of sulphuric acid, by passing the gas through a luted tube at a red heat *.

Though this acid exists in the gaseous state, it can be rendered fluid by combination with water ; 100 grains of water take up 5 grains of the gas ; or, according to Dr Thomson, 8.2 grains, equal to 33 times its volume. The solution has a pungent disagreeable odour, and an acid taste. It reddens some of the vegetable colours, such as that of litmus or red cabbage ; there are others, however, the colour of which it destroys, as that of the red rose. The effect of the gas upon these colours is similar. A singular fact, with regard to its effect on colours, is stated on the authority of Planche, that the blue colour of syrup of violets, which has been changed to a red by any of the acids, is restored by sulphurous acid either in its gaseous or liquid form †.

The saturated solution allows the gas to escape at a moderate heat, and by boiling, the greater part is expelled, though the liquor remains acid, apparently from the presence of sulphuric acid. It is singular that it is not expelled by freezing ; it remains combined with the ice, and renders it so heavy that it sinks in water. This fact shews that this gas has, comparatively with others, little tendency

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* Journal de l'Ecole Polytech. Cah. II. p. 183.

† Nicholson's Journal, vol. xvii. p. 303

to pass into the aëriform state. The freezing of the solution takes place at a few degrees below 32.

The liquid sulphurous acid slowly absorbs oxygen from the atmosphere, and is converted into sulphuric acid.

When two parts of it in the state of gas are mixed with one part of oxygen gas, if the mixture is kept over mercury, they do not act on each other. But if a small portion of water is introduced, they gradually combine and form sulphuric acid, a fact explained on the supposition that the water exerts a strong disposing affinity to this acid. By passing a mixture of oxygen gas and sulphurous acid gas through a tube heated to redness, sulphuric acid is formed. Yet it is singular, that sulphuric acid, transmitted through an ignited tube, is converted, as has been already stated, into sulphurous acid and oxygen gases.

Hydrogen does not act upon this acid at a low temperature, but at that of ignition it attracts its oxygen, as by passing a mixture of the two through a red-hot tube; the sulphur partly combines with a portion of hydrogen, and is partly deposited. Charcoal, at the same temperature, produces in it a similar change; by passing sulphurous acid over ignited charcoal, carbonic acid is produced, and crystallized sulphur deposited. It is not decomposed by phosphorus, and it acts feebly on the metals. It decomposes nitric acid, by attracting part of its oxygen, passing to the state of sulphuric acid, and converting the nitric into nitrous. It takes oxygen, too, from the oxymuriatic acid, and becomes sulphuric acid.

This acid combines with facility with the alkalis, forming salts denominated Sulphites. They differ considerably from the salts formed by the sulphuric acid. Their taste is sulphureous; they are decomposed by a high temperature, their acid being either expelled, or a portion of sulphur being driven off, in which case they become sulphates; they are also decomposed by the greater part of the acids, when the sulphurous acid is disengaged with effervescence; the alkaline sulphites are more soluble than the sulphates in water, the earthy sulphites less so. All these salts are converted into sulphates by exposure to the atmospheric air, or by the action of any substance capable of affording them oxygen. They suffer this change, for example, by deflagration with nitre.

SULPHITE OF POTASSA.—The sulphurous acid unites with potassa with facility, the gas being introduced into a saturated solution of carbonate of potassa in water, until the effervescence from the disengagement of the carbonic acid ceases. The potassa is then saturated with the sulphurous acid, and the neutral salt crystallizes in a short time. Its crystals are white and transparent, and either of a rhomboidal figure, or in the form of small needles running from a centre. Its taste is penetrating and sulphureous. Exposed to the air, it slightly effloresces; it gradually absorbs oxygen, however, and is converted into sulphate of potassa. It is soluble in an equal weight of water at a mean temperature, and in a less quantity of hot water. Exposed to heat, it decrepitates; at a red heat it is decomposed, sulphurous acid fumes are disengaged, a quantity of sulphur is also separated, and the alkali remains combined with a quantity of sulphuric acid. It is decomposed by the greater number of the acids, which combine with its base, and expel the sulphurous acid; the nitrous acid converts the sulphurous into sulphuric, by affording it oxygen, and nitric oxide gas is disengaged. It is likewise decomposed by barytes and lime which attract its acid. It consists, according to Dr Thomson's analysis of it, of 54.5 potassa, 43.5 sulphurous acid, and 2 water.

This salt was long used in medicine under the name of Sal Polychrest, as an aperient. It was prepared by deflagrating equal parts of sulphur and nitre, in a crucible heated to redness. The nitre affording oxygen to the sulphur, converts it into sulphurous acid, which combines with the potassa; there is also, however, a portion of sulphuric acid generally formed, so that this is not a pure sulphite. The process was till lately retained in the Pharmacopœia, but is now expunged, and the preparation is banished from practice, as having no medicinal virtues different from sulphate of potassa.

Sulphite of Soda.—This salt may, like the former, be prepared by saturating a solution of soda with sulphurous acid. It is white and transparent, its taste is cool and somewhat sulphureous, and its crystals are prismatic; they effloresce on exposure to the air, and their acid is converted into sulphuric, by gradually absorbing oxygen. Exposed to heat, it first undergoes the watery fusion, and is then decomposed. It is soluble in 4 parts of water; it requires, however, less warm water, and the latter solution crystallizes on cooling. It consists, in the crystallized state, according to Vauquelin, of 18.8 of soda, 31.2 of acid, and 50 of water.

This salt is affected by the greater number of chemical agents, in the same manner as the former. It is decomposed by potassa, which attracts its acid. It is not put to any use.

Sulphite of Ammonia.—This salt is very soluble in water, requiring less than its own weight of boiling water for its solution. This solution crystallizes on cooling; its crystals being six-sided prisms, acuminated with six planes, white and transparent. Its taste is cool and somewhat sulphureous. Exposed to air it attracts humidity, and passes gradually into a sulphate; it is fused and volatilized by heat without decomposition. It contains 29 of ammonia, 60 of acid, and 11 of water. It is decomposed by all those substances which decompose the former; it is farther decomposed by potassa and soda, and even by magnesia with the assistance of heat.

Sulphite of Barytes is formed by transmitting sulphurous acid over carbonate of barytes, or decomposing any of the sulphites by the addition of a solution of a barytic salt. It is in the form of a powder, or of very small tetraedral crystals; has a taste slightly sulphureous; is scarcely altered by exposure to the air, if it is in a dry state; is as insoluble as the sulphate; is decomposed by heat, sulphur being sublimed from it.

Sulphite of Strontites has not been examined.

Sulphite of Lime is formed by passing sulphurous acid gas through water in which carbonate of lime in powder is diffused: an effervescence takes place from the discharge of the carbonic acid, and, if after this has ceased, the sulphurous acid gas be continued to be transmitted over the powder which remains at the bottom of the vessel, a soluble sulphite of lime is formed, which, after the liquid has been heated, is obtained crystallized in six-sided prisms acuminated by six planes. The properties of this salt have been examined by Fourcroy and Vauquelin *. It has a taste slightly sulphureous; is efflorescent on exposure to the air, and changes very slowly into sulphate: it is less soluble than the sulphate, requiring 800 parts of water for its solution, but is rendered more soluble by an excess of acid. It is decomposed by heat, a portion of sulphur being sublimed from it. It consists, according to the analysis of it by these chemists, of lime 47, sulphurous acid 48, water 5.

Sulphite of Magnesia is formed, by passing sulphurous acid through water in which magnesia is diffused. It is at first in the state of a powder, which is, however, gradually dissolved; and by exposure to the air, it deposites crystals, which are flattened tetraedrons. Its taste is sweetish, and earthy: it is inodorous; is soluble in 20 parts of cold water, and in a smaller quantity of boiling water. It gradually passes into sulphate of magnesia, by exposure to the air, especially when in solution. It consists of 16 magnesia, 39 sulphurous acid, and 45 of water.

Sulphite of Argil.—Sulphurous acid gas passed through water, in which argil is suspended, combines with the argil, and forms a compound, which is insoluble, and which, when dry, is in the state of a white powder, soft to the touch, and having a sulphureous taste.

The Sulphites of Zircon, Glucine, and Ittria, have not been examined.

Sulphureous acid has been used in the arts, from its property of destroying colours, to whiten silks and wool. It is applied by exposing the substance to be whitened, to the fumes of burning sulphur.

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* Nicholson's Journal, 4to, vol. i. p. 365.

SECT. IV.

OF SULPHURETTED HYDROGEN, AND OTHER COMPOUNDS OF SULPHUR AND HYDROGEN.

Sulphur, it is probable, combines with hydrogen in various proportions. Two compounds, capable of being obtained insulated, and possessed of characteristic properties, have been observed; one existing when uncombined in the elastic form, named Sulphuretted Hydrogen; and another, in which the proportion of sulphur is larger, which has been obtained in the liquid state, and which has been distinguished by the appellation of Super-sulphuretted Hydrogen. Besides these, there is reason to believe, that compounds of these principles in other proportions exist; and from recent researches, there is likewise reason to believe, that in some or all of these compounds, oxygen enters into the composition. Their history, and that of the compounds they form with the substances hitherto described, will form the subjects of the present section.

1. Sulphuretted Hydrogen.—This compound was discovered by Scheele, who examined several of its properties: Bergman and Kirwan prosecuted the investigation; Gengembre seems first to have shewn that it is a compound of sulphur and hydrogen, and that it generally owes its origin to the decomposition of water in the processes by which it is formed; and more lately, it has engaged the attention of Berthollet and Vauquelin. It is formed

in various processes, in which its elements are presented to each other in a nascent or in a condensed state.

That which succeeds best, is applying diluted sulphuric or muriatic acid to the compound of sulphur and iron. This compound is prepared for this purpose by exposing to heat in a covered crucible a mixture of one part of sulphur in powder with three parts of iron-filings by weight, until the sulphur is fused and unites with the iron. The temperature rises to ignition, not from any oxidizement, but in consequence of the combination of the iron and sulphur. The sulphuret of iron, when cold, is in the form of a brittle mass, which is easily reduced to powder. One part of it in this state is put into a matrass, to which a bent tube is adapted; two parts of muriatic acid, previously diluted with four parts of water, are poured upon it; an effervescence is soon excited, from the disengagement of sulphuretted hydrogen gas, which may be received over water, as it is not immediately largely absorbed. In this process, the acid, whether it be muriatic or sulphuric, by a disposing affinity enables the iron of the sulphuret of iron to decompose the water, by attracting its oxygen; the hydrogen is disengaged, and being presented in its nascent state to the sulphur of the sulphuret, combines with it, and forms the sulphuretted hydrogen, which passes into the elastic form. It has been affirmed, that a portion of uncombined hydrogen is also disengaged, and mixes with the sulphuretted hydrogen gas. The quantity of this, however, is not considerable, and, at least for any common experimental purpose, the sulphuretted hydrogen procured in this way answers sufficiently well.

It is also obtained, and, as has been supposed, in a state of perfect purity, from solutions in water of the compounds of sulphur with the fixed alkalis, or with some of the earths. When sulphur is combined with potassa, soda, or lime, on dissolving the compound in water, a partial decomposition of the water takes place; one portion of the sulphur combines with part of the oxygen of the water, forming sulphuric acid, which unites with the potassa; another portion of the sulphur unites with the hydrogen of the water, forming sulphuretted hydrogen, which is likewise detained by its affinity to the potassa. But on adding an acid (muriatic acid according to Kirwan's observations answering best) to the solution, or on adding the acid diluted to the solid sulphuret, this combines with this portion of the potassa, and disengages the sulphuretted hydrogen gas. The quantity disengaged, however, is not considerable, and taking place at once, the experiment is not easily managed.

It was by this method, however, that sulphuretted hydrogen was first procured. The compound of sulphur and potassa, from a fancied resemblance of it in colour to the liver of an animal, was named Hepar Sulphuris. Hence the gas disengaged from its solution was named Hepatic Air. Sulphurated Hydrogen was the name given to it at the first translation of the new nomenclature. Sulphuretted Hydrogen, proposed by Mr Chenevix, is to be preferred, as immediately derived from the established generic term, Sulphuret.

It may be observed, that this gas is produced in other modes, as by exposing to a strong heat mixtures of sulphur with vegetable matter, as sugar, oil, and even with pounded charcoal, as Kirwan ascertained; the hydrogen existing in these substances combining with the sulphur; but in these processes there is reason to believe that it is not perfectly pure, or uniform in composition.

The specific gravity of sulphuretted hydrogen gas is 1.36; compared with atmospheric air it is as 1142 to 1000. 100 cubic inches of it, according to Kirwan, weigh about 33 grains. Its smell is extremely fœtid and peculiar, approaching to that denominated putrid, the effluvia disengaged in putrefaction consisting partly of this gas. It extinguishes combustion, and is incapable of supporting animal life. It is inflammable, though not so much so, perhaps, as we should expect from its composition.

It is absorbed by water, the water taking up more than its volume, or 100 cubic inches absorbing, according to Mr Henry, 108. Mr Kirwan observed, that the solubility of sulphuretted hydrogen obtained from different materials is different, which might be owing either to its mixture with other gases, or to the proportion of its elements not being uniform. The water from this impregnation acquires the fœtid smell of the gas, and a very nauseous taste. It is colourless and transparent. Berthollet has stated, in opposition to what has generally been affirmed, that this solution suffers no other change on exposure to the atmosphere than allowing the gas to escape; that when kept in a vessel of atmospheric air, the sulphuretted hydrogen in it suffers no decomposition; and that this gas, dissolved in water, is decomposed by oxygen and its sulphur precipitated, only when it is combined with an alkaline or earthy base, which, by a disposing affinity, promotes their mutual action. Yet Mr Kirwan has affirmed, that sulphuretted hydrogen dissolved in water is decomposed: if even the water by which the sulphuretted hydrogen had been absorbed, had been previously boiled to free it of air, and if the solution were kept in a bottle well stopt, and inverted in quicksilver, in a few days it became turbid, and in a few weeks deposited the greater part of the sulphur *.

In its elastic state, sulphuretted hydrogen does not combine with oxygen at low temperatures, even though they be kept in a state of mixture for a number of days. If a mixture of the two gases, however, or a mixture of the sulphuretted hydrogen gas and atmospheric air, be placed over water, their mutual action is facilitated by its medium, the oxygen combines with the hydrogen, and a thin deposite of sulphur is formed on the sides of the vessel.

At the temperature of ignition the combination is more rapid. If the sulphuretted hydrogen gas be kindled in contact with the atmospheric air, it burns with a blue lambent flame. When previously mixed with one or two parts of atmospheric air it does not detonate, and the combustion of its elements is not complete, part of the sulphur being deposited on the sides of the vessel. When mixed with an equal volume of oxygen gas, and kindled, it inflames with detonation, the products being watery vapour and sulphurous acid, though still part of the sulphur escapes the combustion. The action of sulphurous acid upon it is somewhat singular. If the two gases are mixed together, there is a deposition of sulphur, which is derived from both of them, the oxygen of the acid com-

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* Philosophical Transactions, vol. lxxvi. p. 129.

bining with the hydrogen of the sulphuretted hydrogen, and forming water. Or if sulphurous acid is added to a solution of sulphuretted hydrogen in water, a similar decomposition happens, and the liquid becomes turbid, from the production of sulphur. A mixture of sulphuretted hydrogen gas with an equal measure of nitric oxide gas, burns, as Kirwan observed, when kindled, with a yellow or green lambent flame, and a portion of sulphur is deposited. If the proportion of nitric oxide be two to one of the sulphuretted hydrogen, their mutual action takes place quickly, without ignition: Part of the oxygen is abstracted by the hydrogen, sulphur is deposited, and the residual gas Mr Kirwan found to be nitrous oxide. Nitrous acid added to its watery solution decomposes it, precipitating the sulphur immediately, from the nitric oxide of the nitrous acid affording oxygen to the hydrogen. Oxymuriatic acid gas mixed with sulphuretted hydrogen gas produces a similar decomposition, attended with a deposition of sulphur; and even when transmitted through its watery solution, it first causes a deposition of sulphur, but by continuing the transmission, at length acidifies this sulphur. From this action of oxymuriatic acid gas on sulphuretted hydrogen, Thenard has given the proportion of its constituent parts. To a given weight of the sulphuretted hydrogen gas, absorbed by water, he added oxymuriatic acid gas, in quantity sufficient not only to yield oxygen to the hydrogen, but likewise to the sulphur, so as to convert it into sulphuric acid; he added to the liquid, muriate of barytes, and having collected the sulphate of barytes produced, from the weight of it he calculated the quantity of sulphuric acid thus formed, and from this again, according to the composition of it which he assumed, the portion of sulphur which had been acidified, and which of course had existed in the sulphuretted hydrogen submitted to experiment. As the result which, however, can be regarded only as an approximation, he states the proportions at 70.857 of sulphur, and 29.143 hydrogen *.

Sulphuretted hydrogen has a peculiar action on the metals, either in their pure state or in their saline combinations, and this affords one of its most discriminating characters. It tarnishes them quickly, or communicates shades of yellow, brown, or purple, with a diminution of metallic lustre. Quicksilver or silver suffers this change from it very quickly, and the tarnishing of silver is in general owing to the agency of the small portion of it in animal effluvia. If added to any of the metallic solutions, it immediately produces a precipitate of the metallic oxide, or even in some cases of the metal in combination with the sulphur; generally of a dark shade, but with the different metals of different colours.

There is still to be noticed a part of the history of this agent, extremely singular,—that it is possessed of the properties of an acid. It enters into combination with the alkalis, and forms compounds, some of which are crystallizable; and what is the most distinctive property of an acid, it is capable of changing the vegetable colours, at least those which are more delicate, to a red. If paper, tinged with the infusion of litmus, or with the juice of radish, be immersed in its watery solution, it is immediately reddened. If the gas itself is transmitted through

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* Annales de Chimie, tom. xxxii. p. 267.

infusion of litmus, it immediately reddens it; and that this effect is not owing to any portion of foreign acid suspended in it, Mr Kirwan proved, by shewing, that if it were previously washed with water, the effect was the same, or if passed from an infusion, which it had already reddened, into another portion of fresh infusion, it preserved the same property *. It also decomposes soap, combines with the metallic oxides, and precipitates sulphur from its combinations with potassa or lime. Having these properties, it is scarcely possible to avoid ranking it as an acid; yet no truth appeared to be more fully established in chemistry, than that oxygen is the principle of acidity, and exists in all acids, and it appeared in opposition to a strong and well established analogy, to consider sulphuretted hydrogen as an acid.

It was supposed, too, that there was some room for doubt on this subject. Though the solution of sulphuretted hydrogen reddens some of the vegetable colours, it has been affirmed, that it renders another delicate colour, which is reddened by all the acids,—the syrup of violet, green. And Berthollet, who maintains the opinion of sulphuretted hydrogen being an acid, admits that he is not certain "if its power is sufficiently energetic to produce the neutral state with the alkaline bases †."

In the former edition of this work, I remarked, that if even the acid powers of this substance were unequivocally established, it is not perfectly certain that oxygen does not enter into its composition. In every process in which

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* Philosophical Transactions, vol. lxxvi. p. 128.

† Chemical Statics, vol. ii. p. 86.

it is formed, oxygen is present, and may be afforded. Thus, in the production of it from the alkaline sulphurets, or from the action of a diluted acid on sulphuret of iron; there is a source of oxygen in the decomposition of the water, which, in these cases, uniformly accompanies its formation. The only fact which appears to prove the reverse, is the formation of it by exposing sulphur to heat in hydrogen gas. But this is not well established, nor the nature of the product of such an operation unequivocally determined. Kirwan was unable to form it, by melting sulphur in a vessel containing hydrogen gas; and the Dutch Chemists were equally unsuccessful, either with this method, or by passing hydrogen gas through a tube containing liquid sulphur. And Scheele observed, that although by heating sulphur in hydrogen gas, the gas acquires a fœtid odour, yet it is not, like sulphuretted hydrogen, absorbed by water; and it must therefore have been of a different nature. Hassenfratz has even shewn, that carbonic acid gas or nitrogen gas acquires the same odour, when passed over melted sulphur *, without, however, forming sulphuretted hydrogen. Neither has the analysis of this gas been executed with that accuracy, to preclude the supposition that it is a ternary compound of sulphur, hydrogen and oxygen. In all the analyses of it, no attention has been paid to the possible source of fallacy, that if it contain oxygen, this, when its composition is subverted, may combine with a portion of its hydrogen, and form water. The proportions of its elements have been estimated from experiments, in which the proportion

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* Mémoires de l'Acad. des Sciences, 1786, p. 52.

of sulphur only was directly determined. From this was inferred the proportion of hydrogen, with which this sulphur was combined. But it is obvious, that for any thing proved by such an analysis, oxygen may also have been a constituent principle of it, and the proportion of hydrogen estimated too high. And if oxygen do enter into the composition of sulphuretted hydrogen, it is obvious that a small quantity may communicate to it its acid powers; for we are not to judge of the quantity of oxygen that may be necessary to acidify a compound base, by the quantity that may be necessary to render acid either of its elements; this, the constitution of the vegetable acids, which have all a compound base of carbon and hydrogen, sufficiently demonstrates.

That these conclusions are well founded, and that oxygen does exist in the composition of sulphuretted hydrogen, appears to be established by recent researches, Mr Davy having found that potassium enters into brilliant combustion in this gas. It may probably, therefore, be admitted as an acid of weak power.

Its acid powers appear to be displayed, not only in the properties above enumerated, but also in its combination with the alkalis and earths; these compounds having characters analogous to neutral salts. They are formed very easily, by passing a current of it in its elastic state through the alkaline solution, or through water in which an earth is suspended. A large quantity of the gas is absorbed. The transmission is continued until the liquor is fully saturated; and any excess of sulphuretted hydrogen may be expelled by a moderate heat. They have been supposed to be formed, too, by boiling sulphur with the alkali or earth in water, when from the decomposition of the water, as has been already explained, sulphuretted hydrogen is formed, which combines with the alkaline base, and by evaporation of the filtered solution, and cooling, the compound may be obtained in a crystallized form; or by exposing a mixture of the sulphur and the alkali or earth in a dry state to heat, and afterwards dissolving them in hot water. In these latter modes, however, of forming these compounds, there is always an excess of sulphur.

The compounds of sulphuretted hydrogen with alkailne and earthy bases, and likewise with metallic oxides, were named by Berthollet *Hydro sulfures*,—a term translated into Hydro-sulphurets. Mr Chenevix has objected to this term, that the prefixed syllable, from its derivation, denotes water, and cannot therefore be employed to express a combination of hydrogen. He proposed to use Hydrogenized Sulphuret, as the generic appellation of these compounds. It is preferable, however, to have a single name; and, as I have already observed, an abbreviation of a term may be employed, in forming a compound name of the substance to which it refers, without any reference to the original derivation. The syllable *oxy*, thus, may be used to denote combinations of Oxygen; and *hydro*, that of Hydrogen, without much impropriety.

With regard to the general properties of these combinations, of those at least formed with the alkalis, and with what have been named the alkaline earths, they are abundantly soluble in water, and are crystallizable; the solution is colourless, while the action of the air is excluded; but when it is admitted, a yellow colour is soon acquired, owing to the oxygen of the atmosphere combining with the hydrogen of a portion of the sulphuretted hydrogen, while the sulphur combines with the remaining portion of it, forming a super-sulphuretted hydrogen in union with the base. If the access of the air be still permitted, oxygen continues to be absorbed, part of the sulphur is deposited, and part converted into sulphuric acid, forming with the base a sulphate. If to the solution of the hydro-sulphuret which has not been acted on by the air, an acid be added, sulphuretted hydrogen gas is disengaged, without any deposition of sulphur; while, if it has been previously exposed to the air, sulphur is deposited. These compounds decompose the metallic solutions, throwing down dark-coloured precipitates.

HYDRO-SULPHURET OF POTASSA.—This salt has been particularly examined by Vauquelin *. It is white, and perfectly transparent, resembling by its transparency, and the size of its crystals, sulphate of soda. Their form is that of a tetraedral prism, acuminated with four planes, and likewise that of an hexaedral prism, acuminated with six planes. Its taste is at first alkaline, and afterwards extremely bitter; when dry, it is inodorous; but when liquid, it exhales a fœtid odour. It attracts humidity from the atmosphere, and passes into a liquid of the thickness of syrup. When fluid, it gives a green colour to bodies in contact with it. It is soluble both in water and in alkohol, producing cold in its solution: with acids, it gives rise to a brisk effervescence, without depositing any sulphur. It precipitates the metallic solutions; the preci-

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* Annales de Chimie, tom. xlii. p. 40.

pitates from different metals being of different colours and shades.

Hydro-sulphuret of Soda.—The properties of this compound have likewise been described by Vauquelin *. Like the preceding, it is of a white colour, transparent; crystallized in tetraedral prisms, acuminated by four planes. Its taste is at first acrid and alkaline, soon becoming extremely bitter. It dissolves abundantly in water, and produces cold in dissolving. Its solution is colourless, but gives a green tinge to paper: It has a smell of sulphuretted hydrogen. Acids produce with it a brisk effervescence, and render this odour very strong; but they do not render the liquid turbid. The nitrous and oxymuriatic acids, however, have this effect, and produce a precipitate of sulphur,—owing to their decomposing the sulphuretted hydrogen, by affording oxygen to its hydrogen; while the other acids merely expel it. This salt precipitates all the metallic oxides from their solutions; the precipitates being of various colours. It does not precipitate the earths from their solutions in the acids, with the exception of argil, zircon, and ittria.

The hydro-sulphurets of potassa and of soda, appear, from these descriptions, to be very similar in their properties. Vauquelin has pointed out a chemical test, by which they may be distinguished,—that of adding a few drops of the solution of each to a solution of argil in sulphuric acid; the hydro-sulphuret of potassa gives rise immediately to a crystallization of alum; while that of soda has no such effect.

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* Annales de Chimie, tom. xli. p. 150.

Hydro-sulphuret of Ammonia.—When equal measures of sulphuretted hydrogen, and of ammonia, each in the elastic state, are mixed together, they immediately combine,—a white cloud is produced,—they are almost completely condensed,—and a thin soft deposite is formed on the sides of the vessel, which exhales a penetrating vapour when exposed to the air *. Another combination of sulphuretted hydrogen gas with ammonia is obtained by transmitting it through a solution of ammonia in water; a great part of it is absorbed, the colour becomes of a yellowish green, and at the same time the liquid acquires a very fœtid odour. This forms the hepatized ammonia, introduced by Dr Rollo, as a nauseating and depressing remedy in diseases of increased action, and as such received into the Pharmacopœia. It appears difficult to saturate by this process the ammonia completely, nor has the compound been obtained in a concrete form.

A combination somewhat analogous, which has been long known to chemists, is that named the Fuming Liquor of Boyle. It is prepared, by exposing to heat in a retort a mixture of sulphur, lime, and muriate of ammonia; a liquor distils over, of a yellow colour, which has a sharp fœtid odour, and exhales white vapours. Berthollet submitted it to examination. He collected the product of the distillation in two successive portions. The first he found to be a hydro-sulphuret of ammonia with an excess of ammonia, to which its fuming property appeared to be owing; the white vapours being ammonia, holding a portion of the hydro-sulphuret in solution. The second por-

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* Philosophical Transactions, vol. lxxvi. p. 136.

tion was not fuming; it was of a deeper colour, and appeared to be a hydro-sulphuret, without an excess of ammonia. On adding to it an equal portion of water of ammonia, it became fuming. Muriatic acid added to it, causes a deposition of sulphur, and a disengagement of sulphuretted hydrogen gas *.

Hydro-sulphuret of Barytes. — This compound may be formed by transmitting sulphuretted hydrogen gas through water, in which barytes is suspended: it is abundantly soluble. When barytes and sulphur are boiled together in water, the barytes renders soluble about one-fourth of its weight of sulphur, and a solution is formed of a yellowish red colour, which, when concentrated, deposites crystals of the form of hexaedral prisms. These according to Berthollet consist of hydro-sulphuret of barytes. A similar crystallization is obtained when the residuum of the mixture of sulphate of barytes and charcoal powder, which has been exposed in a covered crucible to a red heat, is lixiviated with boiling water, and the liquor is allowed to cool. It may be supposed that in both cases these crystals consist of sulphuretted hydro-sulphuret of barytes: yet they scarcely appear to contain any excess of sulphur, but to consist of sulphuretted hydrogen and barytes alone, owing probably to the strong affinity between these substances. The solution remaining after the crystallization accordingly contains, what is in conformity to this view, an excess of sulphur. The crystals give out, when acted on by an acid, a large quantity of sulphuret-

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* Annales de Chimie, t. xxv. p. 244.

ted hydrogen. They are white, transparent, and of a silky lustre.

A similar result is obtained from either of these processes with Strontites; and it is probable that the compound is of the same nature.

Hydro-sulphuret of Lime can be formed by transmitting sulphuretted hydrogen gas through water in which lime is suspended. The compound which is formed is capable, as Berthollet discovered, of crystallizing in prisms: it is soluble in water; the solution is without colour, but has a fœtid smell.

Sulphuretted hydrogen transmitted through water in which magnesia is suspended, dissolves a small quantity of it. Its relations to the other earths have not been particularly examined, and its action upon them appears to be weak.

The knowledge which we have acquired of sulphuretted hydrogen, and of its combinations, has thrown light on the composition of the Mineral Sulphureous Waters, and of the changes which they suffer. As sulphur is by itself insoluble in water, and as frequently no traces of an alkali, by which it might be rendered soluble, could be discovered in these waters, chemists found it difficult to conjecture by what means its solution was effected. The discovery of sulphuretted hydrogen, and of its solubility in water, solved this difficulty; and the mutual action exerted between it and oxygen, above explained, elucidate the changes these waters suffer from exposure to the air.

II. SUPER-SULPHURETTED HYDROGEN.—Sulphuretted hydrogen is capable of combining with an additional proportion of sulphur, and there is some reason to believe, as I have already remarked, that this proportion is not determinate, but variable. Mr Kirwan observed, that sulphuretted hydrogen gas formed at a high temperature, deposited sulphur on cooling, which it must therefore have contained in excess. Another compound, which has been more particularly examined, and to which the name of Super-sulphuretted Hydrogen has been more peculiarly appropriated, is one formed when the compound of sulphur with lime or an alkali, dissolved in water, is decomposed by an acid; a liquid being then precipitated of a yellow or reddish colour, having the appearance of oil. But, besides this, other compounds supposed to consist of sulphur and hydrogen have been observed. Lampadius obtained, by exposing to heat a mixture of charcoal and sulphuret of iron, a very volatile liquid, which he supposed to be of this nature. Clement and Desormes, by passing sulphur in vapour over ignited charcoal, obtained a similar product, which they considered as a compound of sulphur and charcoal. But the younger Berthollet has more lately found reason to conclude that it also consists of hydrogen and sulphur. The same chemist, in the course of his researches, obtained other products which he regarded as of similar composition, varying in the proportions of their constituent principles. The chemical history of these compounds remains to be delivered, beginning with that which has been longest known, and the composition of which appears least equivocal, the substance named more peculiarly Super-sulphuretted Hydrogen, and by some chemists Hydroguretted Sulphur.

This compound was first observed by Scheele, and was afterwards examined by Berthollet. It is obtained, as I have remarked above, by adding a large quantity of muriatic acid to a solution of an alkaline sulphuret; or still more readily, by pouring small quantities of the solution into the acid; a little sulphuretted hydrogen gas is disengaged; but while the greater part of the sulphur is precipitated, a portion still remains combined with the remaining sulphuretted hydrogen, forming a liquid which has the appearance of oil, of a yellow or reddish colour, and which soon subsides to the bottom of the vessel. From this compound the sulphuretted hydrogen escapes even at a very moderate temperature, and it is thus ultimately converted into sulphur. The same change is produced in it by the action of the air.

It appears that this substance is capable of combining with the alkalis and earths, or at least that compounds are formed of these, with a combination of sulphur and hydrogen, containing more sulphur than sulphuretted hydrogen; and the principal part of the chemical history of this compound relates to these combinations, its properties in an insulated state having not been examined farther than has been already stated. These compounds are formed directly by boiling an alkaline hydro-sulphuret with a quantity of sulphur, the sulphuretted hydrogen combining with the sulphur, and forming the super-sulphuretted hydrogen which remains in combination with the alkaline base; the liquid becomes of a darker colour. It appears, also, that the solutions of the alkaline sulphurets in water are compounds of this kind. It was formerly known, that when dry sulphuret of potassa, of soda, or of lime, is moistened with water, or dissolved in it, a decomposition of the water, and a production of sulphuric acid and sulphuretted hydrogen, always takes place, this sulphuretted hydrogen being disengaged even by a weak acid, or by the application of heat, while the acid remains in combination with the base [*]. The view, therefore, that was given of the nature of these solutions, was somewhat complicated. On dissolving the sulphuret in water, it was supposed that a portion of the water was immediately decomposed, in consequence of the affinity of the sulphur to its principles, aided by the disposing affinity of the alkali; the oxygen of the portion of decomposed water, combined with one portion of sulphur, forming sulphuric acid, with which a quantity of the alkaline base entered into union; the hydrogen of the decomposed water united with another portion of the sulphur, forming sulphuretted hydrogen, with which another portion of the alkali combined, and thus there existed in the liquid, while it was kept secluded from the atmospheric air, part of the original sulphuret, a quantity of sulphate, and a quantity of hydro-sulphuret, of the alkaline base. The view which has been presented by Berthollet, of the nature of these solutions, is more simple. There can be no doubt, that when they are formed either by dissolving the dry sulphuret of the alkali or earth in water, or, what amounts to the same thing, by boiling the alkali or earth with a portion of sulphur in water, a decomposition of the water takes place, and a portion of a sulphate is formed from the production of sulphuric acid, by the union of the sulphur with the oxygen of the water. But the sulphuretted hydrogen, also produced, instead of being supposed to form a binary compound with a portion of the alkali, leaving a portion of the alkaline sulphuret likewise in the liquor,—according to the view which Berthollet gives, unites with the sulphur and the alkali present, forming of course a compound of super-sulphuretted hydrogen with the alkaline or earthy base. They have been supposed to differ in nothing from the compounds obtained by boiling a hydro-sulphuret with sulphur, except in containing a little of a sulphate which does not appear to modify their properties. They appear, however, to contain less hydrogen and more sulphur; little sulphuretted hydrogen being disengaged when they are decomposed by an acid, while much sulphur is precipitated.

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[*] Mémoires de l'Acad. des Sciences, 1786, p. 55.

These compounds * have a yellow colour, more or less

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* There is much difficulty in forming a proper nomenclature for these various combinations of sulphur with hydrogen, especially in our language. Besides the simple combination of sulphur with a base, to which chemists have agreed to give the generic name of Sulphuret, there are two orders of compounds derived from the combination of sulphur with hydrogen. There is the combination of sulphur and hydrogen in that proportion which forms Sulphuretted Hydrogen, and there is another in which this is combined with an additional dose of sulphur. The former was named by Berthollet, who first attended to these compounds, *Hydogéne Sulfuré;* the second, *Soufre Hydrogéné*, translated, Hydrogenated Sulphur. The compounds formed of the first with alkalis, earths, or metallic oxides, he named *Hydro-sulfures*, (Hydro-sulphurets); those formed of the second with these bases, *Sulfures Hydrogénés*, (Hydrogenated Sulphurets.) This nomenclature, in the English translation,

deep, according to their concentration, but varying also in their tinge from a greenish yellow to an orange red, a fact which undoubtedly proves that they are not uniform

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it must be confessed, is not appropriate, for there is no real distinction between hydro-sulphuret and hydrogenated sulphuret. Mr Chenevix, sensible of this, and considering the term Hydro-sulphuret objectionable, proposed a different nomenclature. The term Sulphuretted Hydrogen he preserves, to denote that compound in which the hydrogen is predominant, or the sulphur in least proportion ; and the other, in which there is an excess of sulphur, he denominates by the name Hydroguretted Sulphur. The compounds which the sulphuretted hydrogen forms, he names Sulphuretted Hydrogurets ; those which are formed by hydroguretted sulphur, are termed Hydroguretted Sulphurets. These terms are no doubt systematic, but they are so harsh, that notwithstanding what Mr Chenevix has urged in their defence, their introduction cannot be admitted but with reluctance. They are also, especially the latter, so much alike, that when using them, it requires some reflection to recollect the distinction between a Sulphuretted Hydroguret and a Hydroguretted Sulphuret. The nomenclature proposed by Mr Kirwan, while it is sufficiently correct and systematic, is free from these objections. Sulphuretted Hydrogen is applied in the sense in which it is universally used, as expressive of the elastic compound in which hydrogen predominates ; and the term Super-sulphuretted Hydrogen very well denotes that compound in which there is an additional proportion of sulphur. Hydro-sulphuret may be applied, as already stated, without impropriety, to the compounds of sulphuretted hydrogen ; the compounds of the other, Mr Kirwan names Super-sulphuretted Hydro-sulphurets : here the term *super* is redundant, and in the text I have therefore used merely sulphuretted. We have thus the gradations of sulphur, sulphuretted hydrogen, super-sulphuretted hydrogen ; with the corresponding names of their combinations,—sulphuret, hydro-sulphuret, and sulphuretted hydro-sulphuret.

in their composition, but differ in the proportions of their constituent parts, principally perhaps in the proportion of the sulphur, but likewise also in the proportion of sulphuretted hydrogen. In proof of this, it has been remarked by Proust, that from these liquors, prepared with different proportions, and with or without the application of heat, the quantities of sulphur precipitated, and of sulphuretted hydrogen disengaged by an acid, are very various *. Their smell is slightly fœtid, derived from the sulphuretted hydrogen. They seem liable to spontaneous decomposition, probably from the re-action of their parts, as, when kept for a length of time secluded from the air, their colour becomes fainter, and sulphur is deposited. They are instantly decomposed by the affusion of an acid which combines with the alkaline or earthy base, disengages the sulphuretted hydrogen gas, and precipitates the sulphur. This precipitated sulphur has a white colour, apparently, as has been already observed, from a small quantity of water combined with it. It was formerly named Lac Sulphuris.

The most important chemical property of these fluids is the facility with which they combine with oxygen in its elastic state. If exposed to oxygen gas, an absorption takes place, and continues until the greater part of the sulphur is converted into sulphuric acid. And the effect is the same when they are exposed to atmospheric air.

The view that was given of the nature of this absorption was formerly complicated. When the sulphuret is first dissolved in the water, it immediately reacts on it, and

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* Journal de Physique, t. lix. p. 266.

quantities of sulphuretted hydrogen and of sulphuric acid are formed, which enter into union with portions of the base of the sulphuret. If exposed to the air, the hydrogen of the sulphuretted hydrogen was supposed to attract the oxygen. The sulphur, however, was not precipitated, as the base with which the sulphuretted hydrogen had been combined was able to attract it; a portion of the original sulphuret was therefore reproduced; this reacted on the water, decomposed a new portion of it, producing, by the union of the oxygen with the sulphur, another quantity of sulphuric acid, and, by the union of the hydrogen, another portion of sulphuretted hydrogen; the air being still admitted, the absorption of the oxygen from the agency of the hydrogen of the sulphuretted hydrogen still took place; and these successive changes, it was supposed, went on, until the whole of the sulphur was converted into sulphuric acid, and the liquor was nothing but a solution of sulphate. The view now given by Berthollet is much more simple, and is probably just. Sulphur, from its state of cohesion and insolubility, is incapable of combining with oxygen at a low temperature; in diminishing the cohesion, by raising the temperature, although this obstacle is in part withdrawn, yet a considerable elevation of temperature is requisite to diminish it sufficiently to permit the exertion of their mutual attraction, especially as at the same time the elasticity of the oxygen is increased by the action of the caloric. But when sulphur is combined with an alkali or earth, so as to form a soluble compound, it gains the advantage of fluidity without this increase in the elasticity of the oxygen gas, which would counteract their affinity. Hence, at this low temperature, the combination of sulphur and oxygen, under these circumstances, can take place with as much facility as when the sulphur is melted by heat alone; and the combination may even be promoted by the affinity likewise exerted by the alkali or earth present, to each. The hydrogen of the sulphuretted hydrogen in the liquor may likewise attract oxygen, and accelerate the effect *.

From this property of these combinations, they have been applied to the purpose of eudiometry, and perhaps afford, on the whole, the most simple and accurate eudiometer. The sulphuretted hydro-sulphuret of potassa, or of lime, has been generally employed. The former is prepared by either dissolving one part of the solid sulphuret

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* From the observations of Dr Austin *, compared with the experiment of Scheele already stated, on the analysis of the atmospheric air, by the action of the solution of sulphuretted hydro-sulphuret of potassa, there is reason to believe, that when atmospheric air is long exposed to these liquors, after its oxygen is abstracted, there is an absorption of nitrogen, which combining with the hydrogen of the sulphuretted hydrogen, forms ammonia; or rather perhaps the small portion of nitrogen gas, which will be absorbed by these in common with all watery liquids, enters in this condensed state into combination with the hydrogen, a new quantity will be absorbed, and thus the combination may proceed slowly until even the whole of the nitrogen, if exposed sufficiently long, is consumed. The observation of De Marti, too, already stated, that aëriform fluids absorbed by water, continue to be condensed, and therefore absorbed in larger quantity, as they are exposed to it for a longer time, may account for the great diminution of volume which Scheele observed when atmospheric air was kept for weeks in contact with these sulphuretted solutions.

* Philosophical Transactions, vol. lxxviii.

in 5 or 6 of water, or by boiling one part of sulphur with three parts of the solution of potassa of the common strength, and 4 or 5 parts of water; and, after due boiling, closing the vessel, and allowing the undissolved sulphur to subside. The latter is prepared by boiling equal weights of lime and sulphur in 10 or 12 times their weight of water, for half an hour, and pouring off the liquor, which is of a deep yellow or green colour, from the undissolved matter.

The mode in which the experiment was formerly made with either of these liquors was simple, but defective. It consisted in placing a tube, graduated into 100 equal parts, and containing atmospheric air, into the liquid, taking care to introduce it in such a manner that none of the air should be displaced or be expelled by the heat of the hand. In proportion as the oxygen of the air was absorbed, the liquid rose in the tube; the experiment was continued until the liquor became stationary; it was then only necessary to bring the liquid within and without the jar to the same level, and to make the correction for any variation of temperature, or atmospheric pressure, if necessary; the volume of the residual gas, compared with the original volume, shewed the quantity of oxygen that had been contained in the air submitted to trial.

The great objection to this method of operating, was its slowness. The oxygen is absorbed by the liquid imperceptibly, and when the surface exposed is inconsiderable, as is the case in this mode of experimenting, two or three days elapse before the absorption is complete, independent of the time which is requisite to ascertain that it is so, which amounts to at least 5 or 6 hours.

It has, therefore, always been a desideratum to accelerate the absorption, by using an apparatus which shall present a large surface, renewed quickly by agitation of the liquid, to the air. De Marti, for this purpose, used a tube graduated into 100 parts, by which the air could be measured; this measure of the air subjected to experiment, was introduced into a flask filled with the solution prepared from sulphuret of potassa or sulphuret of lime, and having a stopper adapted to it by which it could be accurately closed. The air being strongly agitated with the liquor for five minutes, was again transferred, in the pneumatic trough, into the graduated tube filled with water, and the diminution of volume which it sustained was thus ascertained *.

The apparatus which Dr Hope introduced, is much superior, and unites indeed every advantage. It consists (fig. 46.) of a small bottle designed to contain the sulphuretted solution; to the mouth of this is accurately adapted by grinding, a tube divided into 100 equal parts, and towards the bottom of the bottle is an orifice fitted accurately with a stopper. The bottle being filled with the solution, and its orifice being covered with a flat plate of glass, it is to be placed under the surface of water, and the graduated tube containing the atmospheric air, or whatever gas may be subjected to trial, is inserted into it. The apparatus is then removed from the water, is inclined so as to allow part of the liquor to flow into the tube, and agitated strongly. It is replaced in the water, and the stopper at the under orifice withdrawn, when, of course, from the absorp-

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* Journal de Physique, tom. lii. p. 177.

tion of the oxygen of the air, a quantity of water rushes in. The stopper is again introduced, the agitation renewed, and the operation is thus repeated until the absorption proceeds no farther. The amount of this may be determined by plunging the bottle with the tube adapted to it into water, removing the stopper of the under orifice, and taking care that the water without is at the same level as the liquor within, allowing it also to stand for a short time, that any slight rise of temperature from the application of the hand during the agitation may have ceased.

The diminution which atmospheric air suffers when subjected to this eudiometrical method, is between 21 and 22 in 100. Generally speaking, it is perhaps to be preferred to every other, as of easiest execution, and requiring fewest precautions, or corrections for error. The only fallacy to which it can be supposed subject, is the absorption of a small quantity of nitrogen gas. If it has been newly prepared by boiling, and, if used without previous exposure to the air, it will, in common with any other watery liquid, absorb a portion of the atmospheric air undecomposed, or of its nitrogen as well as of its oxygen, and probably the substances with which it is impregnated may even render the absorption of nitrogen rather greater than it would be by pure water. Accordingly, under these circumstances, nitrogen is absorbed by these liquids, and even in large quantity, when the proportion of liquid to the air is considerable, as De Marti shewed by experiment. Having prepared a sulphuretted hydro-sulphuret of lime by boiling, and having cooled it without exposure to the atmosphere, and agitated 1 measure of atmospheric air with 20 measures of this liquid, he found the diminution to amount to 50 in 100, so that here 29 of nitrogen gas had been absorbed *. Berthollet, on making the experiment, did not find this absorption of nitrogen; but he had operated with a sulphuretted liquid prepared in the cold. Humboldt and Gay Lussac, on repeating the experiment of De Marti, obtained a similar result, the absorption of nitrogen being greater, as was to be expected, as the proportion of liquid was greater to that of the atmospheric air employed; so that in one experiment the diminution of volume which atmospheric air sustained was 23, in a second 23.6, and in a third 26 †. There can be no doubt, therefore, of the absorption of nitrogen by these liquids, and of its cause,—that when the liquid has been made to boil, the air it contained had been expelled, and that, in common with all watery liquids, when again exposed to atmospheric air, it would absorb a portion of it undecomposed, this being greater in proportion to the quantity of liquid.

There seems reason to believe also, as has been already observed, that the portion of nitrogen thus condensed in these liquors enters slowly into combination with the hydrogen of the sulphuretted hydrogen, and thus a fresh quantity will be successively absorbed. Hence the result in Scheele's experiments, that when atmospheric air was exposed to their action for two weeks, the diminution of volume amounted to 27 or 28 in 100.

These sources of error, however, are easily guarded against. To obviate the first, the liquor, if newly prepa-

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* Journal de Physique, tom. lii. p. 178.

† Ibid. tom. lx. p 132.

red, ought, before it is used, to be agitated for a short time with a quantity of atmospheric air, that it may imbibe as much nitrogen gas as it can receive; and in operating with it, any error will be more completely avoided by not using too large a quantity of liquid, the proportion ought not perhaps to exceed 4 or 5 to 1 of atmospheric air by measure. With regard to the second, when the preceding method, in which the absorption of oxygen is so much accelerated, is used, there can be no error, as the combination of the nitrogen of the hydrogen takes place very slowly. The residual air has a slightly fœtid smell, which might be ascribed to sulphuretted hydrogen; the presence of which, therefore, might be supposed a source of error; but if present, it is in a quantity altogether inappreciable, as, by washing the air with water, this odour is removed, without any perceptible diminution of volume. Of the two liquors which have been employed, the sulphuretted hydro-sulphuret of lime, and of potassa, the former is more economical, and appears to be rather more active. With either of them, however, this, on the whole, appears to afford the best eudiometrical process; it is least troublesome, subject to fewest errors, and requires the simplest apparatus.

THE properties of SULPHURETTED HYDRO-SULPHURET OF POTASSA, as well as its preparation, have been described in the general account now given of these combinations. Obtained by boiling solution of potassa on sulphur, it is of a yellow colour, of various shades, from its state of concentration, and probably also from variations in the proportion of sulphur. Its taste is nauseous and acrid, it has a soapy feel, and stains the cuticle black. It is decomposed by the acids, which precipitate the sulphur white or of a pale yellow, and disengage a portion of sulphuretted hydrogen gas. By long exposure to the air, the sulphur, by absorbing oxygen, pasess to the state of sulphuric acid, and the liquor affords sulphate of potassa.

The SULPHURETTED HYDRO-SULPHURET OF SODA has properties perfectly similar, at least no distinction has been established between them. From long exposure to the air it will afford sulphate of Soda.

SULPHURETTED HYDRO SULPHURET OF AMMONIA. This compound is formed by adding to the hydro-sulphuret of ammonia a portion of sulphur, which it dissolves in considerable quantity even in the cold. It has a deep yellow colour, and an oily consistence: It is decomposed by exposure to the air, the oxygen of which combines with its hydrogen, and causes a deposition of sulphur.

SULPHURETTED HYDRO-SULPHURET OF BARYTES. This compound, I have already remarked, is obtained by boiling barytes with one-fourth of its weight of sulphur in water; a solution being formed of a yellowish red colour and a fœtid smell, which is the proper sulphuretted hydro-sulphuret of this earth. The colourless crystals which it deposites, I have already stated, are supposed to be a hydro-sulphuret. From strontites boiled with sulphur, a similar solution is obtained.

SULPHURETTED HYDRO-SULPHURET OF LIME. This compound is formed when sulphuret of lime is dissolved in water, or with less trouble, by boiling lime with a third of its weight of sulphur, and ten times its weight of water. The solution is of an orange red colour, has a fœtid smell, and resembles in the chemical actions it exerts, the analogous combinations of sulphur with the fixed alkalis.

Sulphuretted Hydro-Sulphuret of Magnesia is the only other combination of this kind among the earths, and even it appears to be imperfectly established; a liquor having only a faint yellow colour, and a slightly fœtid smell being formed, when magnesia and sulphur are boiled together in water, or when they are exposed to heat in a crucible, and afterwards dissolved in water.

Besides the compounds of sulphur with hydrogen which have been described, there is reason to believe, as I have already remarked, that some others can be formed; and the substances supposed to be of this nature still remain to be considered.

Lampadius of Freyberg in exposing to heat a mixture of native sulphuret of iron and charcoal, obtained a liquid extremely volatile, having a sulphureous smell, inflammable, and which he supposed to be a compound of sulphur and hydrogen. He was unable again to form it, though he frequently repeated his experiment. At length, after an interval of some years, performing some experiments on wood impregnated with pyrites or sulphuret of iron, he succeeded, and has given several methods by which it may be obtained. The general process consists in either exposing pyritized wood alone, or a mixture of pyrites with common or bituminous wood, fossil wood, or anthracite, to a strong heat in an earthen retort, connected with an adopter, the extremity of which dips in a vessel of water. A large quantity of sulphuretted hydrogen gas is disengaged (except when anthracite is employed) with a little empyreumatic oil, and as soon as the retort is at a full red heat, this peculiar product, which Lampadius from its volatility calls alkohol of sulphur, passes over in small liquid drops which fall to the bottom of the water. When anthracite is employed, it is white, and contains no empyreumatic oil, with which it is always tainted when the other substances are used. To separate this oil, it is again distilled by a lamp heat in a retort with a little water, the extremity of the neck of the retort being immersed in distilled water. It is thus obtained perfectly white*.

The properties of this substance are extremely singular as described by Lampadius. It has a penetrating odour; is highly volatile, boiling at 104°, and in its evaporation producing a great degree of cold; it is heavier, however, than water, its specific gravity being 1300; it is exceedingly inflammable, burns with a blue flame and without smoke, or without any residuum; the products are sulphuric acid and a little water. It is soluble abundantly in alkohol, but very sparingly in water; it dissolves phosphorus readily, and without the assistance of heat.

From its production and properties, and in particular from the products of its combustion, this substance, it may be concluded, is a compound of sulphur and hydrogen. Some doubt however existed with regard to this, as Lampadius did not appear to have analysed it with much accuracy, and Clement and Desormes, in experiments made to investigate the nature of charcoal, obtained a product very similar, which they considered as a compound of charcoal and sulphur. The process they gave to obtain this carburetted sulphur, as they named it, is to pass sulphur in vapour through an ignited porcelain tube, in which charcoal in fragments and in powder has been previously heated; this previous heat must have been applied until the production of the elastic fluid, which charcoal from heat alone gives out, has ceased; the sulphur is then introduced slowly. When it acts on the charcoal, a yellowish liquid, having the appearance of an oil, condenses in the vessel adapted to the tube; it may be received in water, through which, from its greater specific gravity, it falls in globules, and is collected at the bottom. No gas, it is added, is produced in this process; and though there is some difficulty in conducting it, in one experiment which they made, they succeeded so far, that ten grammes of charcoal disappeared. If the proportion of sulphur is larger, the product is concrete, and crystallizes in the receiver.

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* Philosophical Magazine, vol. xx. p. 131.

The liquid product they describe as "transparent and colourness when pure, but having in general a greenish yellow colour; it has a disagreeable odour, somewhat pungent, but not insipid like that of sulphuretted hydrogen; it produces on the skin a considerable degree of cold, and evaporates as speedily as ether, without any residuum if colourless, and leaving sulphur behind it, if yellow. Its taste is at first cool, but afterwards pungent like that of ether. It is heavier than water in the proportion of 13 to 10." They have shewn, by several experiments, that it is different in its properties from super-sulphuretted hydrogen. It is not even soluble in water; but when placed in a vacuum rises through it in the elastic state, and when pressure is applied, re-appears in the liquid form;

nor when in this gaseous state does it blacken acetite of lead. It inflames with facility, gives a smell of sulphurous acid, deposites sulphur, and leaves a residuum of charcoal; its vapour, diffused in oxygen gas or nitrous gas, when kindled, burns with detonation. It can unite with more sulphur, becoming deeper coloured, but does not act on charcoal. It unites with ammonia, with potassa, and soda; it also unites with oil, with a slight deposition of charcoal from decomposition. It is not altered by the nitric, muriatic, and sulphuric acids, when cold; but is partially oxidized by the nitric acid aided by heat, and also by the liquid oxymuriatic acid even in the cold *.

This substance agrees with that described by Lampadius in the greater number of its properties. Is it, then, a compound of sulphur and hydrogen, or of sulphur and charcoal? Had it not been from the positive assertion, that charcoal disappears in its formation, and that it deposites charcoal in its combustion, the latter opinion would scarcely have been received; for it is a very improbable supposition which it involves, that two substances, such as sulphur and charcoal, which are comparatively fixed and dense, should form by their union a substance so volatile and light; and even if charcoal did exist in its composition, the most probable conjecture with regard to its composition would have been, that it is a ternary compound of carbon, hydrogen, and oxygen. It has lately, however, been more minutely examined, and the conclusion has been drawn, from the experiments made with regard to it, that it is a compound of sulphur and hydrogen.

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* Philosophical Magazine, vol. xiii. p. 156.

Berthollet *junior* first submitted this question to examination. He repeated the process indicated by Clement and Desormes, with some slight modifications in the apparatus. A coated tube of glass was placed a little inclined across a furnace, connected at the lower end by an adopter with a tubulated receiver, from which a curved tube passed into water in a two-necked bottle, and from this another bent tube conveyed any elastic fluid into the pneumatic apparatus. Some pieces of charcoal were placed in the middle of the tube, which had been previously exposed to a red heat for half an hour, to expel any aërial matter. A little sulphur was placed at the upper end, and this was then closed by melting the glass. The part of the tube in which the charcoal lay, was then heated to incandescence; and a gentle heat was applied to the part which contained the sulphur, so as to melt it, and cause it to run down on the charcoal. As soon as they came in contact, bubbles of gas were disengaged rapidly, accompanied with white vapours, which condensed in the receiver, and appeared at the bottom of the water contained in it, in the form of an oily-like fluid, white, or sometimes yellowish. When it is wished to produce much of this liquid, Berthollet found that it is necessary to keep the charcoal at a red heat, and to pass over it only a slight excess of sulphur, and to keep the receiver cool. If too little sulphur pass over, there is no product but of a gas, and a few drops of a liquid, which floats on the surface of the water, and which in the course of the experiment resumes the gaseous state. If too much sulphur pass the effects are similar, and there besides condenses in the adopter much of the solid product which had been observed by Clement and Desormes.

The several products of these operations were examined by Berthollet. The water in the bottle through which the gas had passed was milky, and had the smell, and all the characters of water impregnated with sulphuretted hydrogen. The gas had the same odour. Agitated, or left in contact with water, it was absorbed, and communicated to it this odour. It burned with a blue flame, exhaling an odour of sulphurous acid. Mingled with oxygen it detonated strongly by the electric spark, sometimes without affecting lime-water, at other times producing in it a light precipitate. We recognise in these characters those of sulphuretted hydrogen, only this gas is rather less soluble in water than that produced by the usual methods. But this is not peculiar to it. Scheele, as has been already remarked, by heating sulphur in hydrogen, obtained a gas having the fœtid odour of sulphuretted hydrogen, but little soluble in water; and Kirwan, who had obtained varieties of sulphuretted hydrogen by different processes, observed, that they differed considerably in the degree of their solubility in water *. The younger Chaptal, too, found considerable differences in the solubility of different gases of this kind,—proofs sufficient of the different proportions in which these principles may unite.

The liquid collected under the water in the receiver had all the characters of the substance described by Lampadius, and by Clement and Desormes. It was nearly as transparent as water; had a smell similar to that of sulphuretted hydrogen, but rather more brisk and pungent; shaken in a phial it adhered to the sides like oil: it burn-

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* Philosophical Transactions, vol. lxxvi. p. 129.

ed brightly with a blue flame, and a smell of sulphurous acid : it is extremely volatile, producing a sensation of cold on the skin as it evaporates ; exposed under a jar to atmospheric air, it greatly enlarges its volume, and the air burns, when kindled, with a blue flame, without detonation; but it detonates violently when mixed with oxygen.

The most important point was to determine its composition. Berthollet found, that in its combustion it was entirely consumed, without leaving any trace of charcoal, as Clement and Desormes had affirmed. If its combustion were stopt, the residuum appeared to be sulphur. Sulphur remained, too, on the evaporation of this liquid, but neither did this give any trace of charcoal. The elastic products of its combustion were examined, but in these also no indication of carbonic acid could be found; limewater not being rendered milky when the vapour of it mixed with oxygen was detonated over it. In decomposing it by oxymuriatic acid, sulphur is deposited, but neither charcoal nor carbonic acid appears. In combining it with an alkaline liquor, a sulphuretted hydro-sulphuret, without any residuum of charcoal, is formed. From all these facts Berthollet concludes, that this liquid is, as Lampadius had conjectured, a compound of sulphur and hydrogen. The hydrogen existing in it he supposes to be derived both from the sulphur and charcoal *.

Robiquet, assisted by Vauquelin, had also made experiments on this substance. They obtained it by a similar process ; its physical properties, as described by them, are

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* Mémoires de la Société d'Arcueil, tom. i. p. 304. ; or abstract in Nicholson's Journal, vol. xviii. p. 43.

nearly the same as have been stated above; and the account of its chemical relations agrees nearly with that by Clement and Desormes. Its watery solution precipitates several of the metallic solutions, particularly those of lead of an orange yellow, mercury white, and tin a reddish yellow: it does not redden litmus. Concentrated sulphuric acid has little effect on it. Nitric acid and oxymuriatic acid decompose it. Pure potassa combines with it, but not very rapidly: ammonia and barytes dissolve it more easily; and these solutions precipitate a number of metallic salts. These chemists could discover nothing to indicate the presence of carbon in this substance *.

Berthollet, in the course of his experiments, obtained results from which the existence of other compounds of sulphur and hydrogen in different proportions might be inferred; and he has supposed, that the predominating ingredient in these combinations communicates to the compound some of its properties. If the sulphur be abundant, it assumes the solid form; if the proportion of hydrogen be increased, it exists as a liquid; and if still farther augmented, it assumes the elastic form.

In distilling the liquid above described with water at a heat of 112°, a gas was obtained, having the odour of sulphuretted hydrogen, and its general properties. A liquid then came over colourless, lighter than water, and very volatile. As the temperature increased, and the production of gas ceased, this had evidently more density, and at length was heavier than water, and had become yellow and more opaque. On stopping the process, what remained in the retort became solid by cooling, and pris-

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* Philosophical Magazine, vol. xxx. p. 30.

matic crystals were formed in the mass. These facts sufficiently confirm the above view. In distilling sulphur, too, over charcoal, liquids of different densities are obtained, according as the temperature regulates the proportions. And if there be a great excess of sulphur, a solid compound, as has already been remarked, is obtained. This appears to contain very little hydrogen. It has a laminated texture, a density inferior to that of sulphur, and a fœtid smell, and, when heated, gives out sulphuretted hydrogen, without affording any charcoal. It is therefore solid hydrogenated sulphur. He also states, that when the sulphuretted hydro-sulphurets are decomposed by acids, the sulphur which is precipitated retains a portion of hydrogen.

Berthollet adds, that when the temperature is strongly raised, and much sulphur is made to pass, the charcoal disappears, and enters into the composition of the elastic fluid. A triple compound of carbon, hydrogen, and sulphur, therefore, exists, which is afterwards to be noticed.

It is not very obvious what relations the products that have been described have to the super-sulphuretted hydrogen, obtained in the decomposition of the sulphuretted hydro-sulphurets by an acid. As this has an oily appearance, and a yellow colour, it is not improbable that it is similar to some of the more dense and coloured liquids, described as obtained in the above experiments.

It still remains to be determined, too, whether these compounds contain oxygen; for it is obvious that the circumstances of their formation, or the products of their analysis, as it has been hitherto executed, do not preclude the presence of this element; nor indeed have the proportions of their constituent parts been assigned.

SECT. V.

OF THE COMPOUNDS OF SULPHUR WITH THE ALKALIS AND EARTHS.

Sulphur combines with the fixed alkalis, and with several of the earths, forming sulphurets, of which the chemical history remains to be given.

These compounds are formed by exposing the alkali or earth, with the due proportion of sulphur, to a moderate heat in a covered crucible. They exist only in the solid form; for when dissolved in water new combinations are established, as has been already explained; a super-sulphuretted hydrogen is formed, and of course a sulphuretted hydro-sulphuret exists in the liquor. In the composition of this, however, only a small quantity of hydrogen exists; for when these solutions are decomposed by an acid, there is a copious precipitation of sulphur, and but little disengagement of sulphuretted hydrogen gas. Frequently even there is no sensible effervescence; and the odour only of this gas becomes perceptible. According to Berthollet, however, the sulphur which is precipitated contains a portion of hydrogen; but whether more than in common sulphur he does not appear to have accurately determined. The properties of these solutions and their application to eudiometry have been already stated.

Sulphuret of Potassa.—This compound is formed by exposing to heat in a covered crucible, equal parts by weight of sulphur and dry concrete potassa; their combination takes place quickly, and the compound is fused.

When it has become concrete, it is firm and brittle, of a dark reddish-brown colour, which from its resemblance to the liver of an animal gave origin to the name of Hepar Sulphuris, given by the older chemists to these compounds. A similar combination is obtained, by exposing to heat one part of sulphur, with two parts of sub-carbonate of potassa, the sulphur and the alkali uniting, and the carbonic acid being expelled, as Mr Kirwan found by experiment *. The combination appears to be less intimate, however, probably from part of the carbonic acid being retained, as the colour is only grey or green.

Sulphuret of potassa is perfectly inodorous while it remains dry; it is only when either moistened or dissolved that it acquires a fœtid smell, from the production of sulphuretted hydrogen. It is fusible, and when exposed to a strong heat in close vessels, a portion of sulphur is sublimed from it, without any sulphuretted hydrogen gas, while a portion of this gas is obtained in this experiment, if the sulphuret has been previously moistened †. Exposed to the air, it attracts humidity, especially that which has been prepared with pure potassa, probably from an excess of alkali. From this substance always suffering a chemical change when in a state of solution, it is scarcely possible to discover precisely its peculiar agencies. One singular property belonging to it, is, that when fused with some of the metals, with gold for example, a combination is formed, which is soluble in water, a fact observed by Stahl, and not yet fully elucidated.

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* Philosophical Transactions, vol. lxxvi. p. 120.

† Mémoires de l'Acad. des Sciences, 1786, p. 53.

SULPHURET OF SODA has not been particularly examined. It is formed by the same process as sulphuret of potassa, and has been described as being perfectly similar in appearance.

SULPHURET OF AMMONIA does not appear to exist, as there is no mode of bringing its elements to act on each other, without the presence of sulphuretted hydrogen, which forms a hydro-sulphuret.

SULPHURET OF BARYTES is formed by exposing sulphur and barytes to a red heat in a covered crucible, the compound having a reddish-yellow colour. SULPHURET OF STRONTITES is formed by a similar process, as can also the SULPHURET OF LIME; and in external appearance they are nearly the same. The sulphurets of the other earths are not known.

SULPHUR appears capable of combining with the bases of the alkalis and earths. Mr Davy found that it unites readily with potassium, when they are brought into contact in tubes filled with the vapour of naphtha; there is a rapid evolution of heat and light, and a gray substance in appearance like artificial sulphuret of iron is formed: a little sulphuretted hydrogen is formed at the moment of combination, no doubt from the hydrogen of the sulphur. This sulphuretted potassium easily inflames; it is also gradually oxygenated from exposure to the air, and converted into sulphate of potassa. Sodium and sulphur combine with equal facility, heat and light being disengaged, and sometimes an explosion produced from the vaporization of a portion of sulphur, and the disengagement of sulphuretted hydrogen. The compound is of a deep gray colour.

The phenomena displayed in these combinations are similar to those which attend the combinations of sulphur with the metals; and the compounds have properties similar to the metallic sulphurets.

The combinations of sulphur with the other inflammables, and with the metals, will be taken notice of under the history of these substances.

CHAP. III.

OF CARBONIC ACID, AND ITS BASE.

THE first important discovery in Pneumatic Chemistry was that by Dr Black, of an aëriform fluid existing in combination with the alkalis and some of the earths, and capable of being disengaged from them, so as to be obtained in an insulated form. To this elastic fluid Dr Black gave the name of Fixed Air, and he ascertained its principal properties. Bewly and Bergman afterwards discovered that it is an acid, and, being known to exist in the atmosphere, it received the name of Aërial Acid. It was also known to be produced in the combustion of charcoal; and at the framing of the new nomenclature, the term Carbon being introduced to denote the pure inflammable matter of charcoal, this product of its oxygenation was named Carbonic Acid. Carbon, like sulphur, exists in various states of combinations, forming several important compounds. Its purest form, perhaps, is the Diamond; for this valuable gem is not only an inflammable body, but, it has been amply demonstrated, affords, in burning, precisely the same product as common charcoal. The mineral known by the name of Plumbago consists also principally of carbonaceous matter. In Charcoal the simple base has been supposed, by some chemists, to be combined with oxygen; by others with hydrogen. When charcoal receives a certain portion of oxygen, it is converted into an elastic fluid, which, having no acid properties, has been named Carbonic Oxide; and when it is fully oxygenated, it forms, as has been already remarked, Carbonic Acid. There exist, besides, several compound gases, of which carbon is the base, combined with hydrogen, and probably with oxygen. The history of all these substances forms the subject of the present chapter.

It is not certain if we have yet obtained the substance which is their common ingredient, or primary base. At one time charcoal was supposed to be this base. It always contains, however, a little saline and earthy matter, and there is further reason to believe that it contains hydrogen, and perhaps oxygen. The Diamond was afterwards supposed to be pure carbon, but it, too, according to Mr Davy, contains a small quantity of oxygen. In plumbago, iron was known to be contained; and, according to the same chemist, it is a compound of carbon and iron. If these views be correct, therefore, the pure inflammable base of all these substances, that to which the name carbon is understood to be appropriated, has not been obtained in a perfectly insulated form. It is convenient, however, to have a term by which it can be designated; and in diamond, and well calcined charcoal, it is probably not far from being in a pure state. It is a chemical principle of much importance, carbonaceous matter being the principal ingredient of all vegetable, and of many animal substances, besides being extensively distributed in the mineral kingdom. Diamond may first be considered as its purest form.

SECT. I.

OF DIAMOND.

The Diamond has always been regarded as the most valuable of the gems, and consequently as the most valuable production of the mineral world, a superiority which it derives from its very high lustre and hardness. The first quality arises from its greater refractive power, which is such as to cause all the light to be reflected which falls on it at an angle of incidence greater than of 24½ degrees; and it is capable of being rendered still more brilliant by its surface being cut into facets, which multiply the reflections of light. From its hardness, too, its lustre remains uninjured: This hardness is such, that it can be cut, or rather worn down only by rubbing one diamond against another, and is polished only by the finer diamond powder. It occurs crystallized, either in perfect crystals or fragments, is colourless or tinged of various shades, generally transparent, of a laminated structure, and having a specific gravity of from 3.5 to 3.6. It is found in India, and in Brazil.

The diamond is phosphorescent, or, when it has been exposed to the light, is luminous in the dark. It becomes electrical on rubbing, the electricity being positive.

From the qualities of the diamond, it was long ranked with the other gems, and considered as analogous to them in its chemical constitution. Newton, by a happy application of a physical principle, conjectured that it is an inflammable substance. Transparent bodies which are uninflammable refract light nearly in the ratio of their density, while those which are inflammable have refractive powers which are greater than their densities; and the diamond having this great refractive power, led Newton to conclude, that it "probably is an unctuous substance coagulated *." In 1695, experiments had been made at Florence, which proved the diamond to be dissipated by the intense heat in the focus of the powerful burning lens of Tschirnausen. Afterwards, in experiments made at Vienna, it was found, that in the heat of a furnace, diamonds lost weight, and, if exposed for a sufficient length of time, entirely disappeared, while the ruby and other gems exposed to the same heat remained unaltered. At a latter period, Darcet exposed diamonds to heat inclosed in balls of porcelain clay in various ways, and always found that they were dissipated by exposure to a strong heat. These facts, at the same time, appeared in contradiction to the common practice of the jewellers, who expose diamonds which are foul, to a strong heat, imbedded

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* Optics, Book II. Prop. 10.

in charcoal to render them clear. An observation of Macquer first threw light on the subject. He took notice, that while the diamond was exposed to a strong heat under a muffle, and while it was losing weight, it was luminous or appeared to burn, a fact which he verified by subsequent experiments. It cannot be doubted, therefore, that in the experiments of Darcet, air had been admitted to the diamonds from rents in the porcelain clay balls in which they were inclosed, and that in the method of the jewellers, they are protected from the action of the air by the charcoal dust with which they are surrounded.

Still a degree of uncertainty was attached to the subject; and to remove this, Lavoisier, associating with him in the investigation Macquer and Cadet, undertook some experiments. They first ascertained, that in close vessels the diamond does not evaporate; having exposed 19$\frac{5}{6}$ grains in a luted earthen retort connected with a glass receiver, and the joining secured, to a very strong heat, the loss of weight amounted only to about 2 grains; yet the heat applied was much higher and continued longer than would have been necessary to dissipate the entire quantity of diamond in the open air; and repeating the experiment of the jewellers, they found that when carefully imbedded in charcoal powder from which the air was excluded, the most violent heat produced no change in the diamonds submitted to trial. They were therefore disposed to conclude, that the dissipation of the diamond, when heated in the open air, is owing to its combustion *. Facts similar to these were established by a second series of experiments perform-

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* Mémoires de l'Acad. des Sciences, 1772, p. 350.

ed by Darcet with Rouelle. And Lavoisier, in another memoir, demonstrated more decisively the combustibility of the diamond, and discovered the product of its combustion. When suddenly heated by a lens, he found it to decrepitate, and to be thrown into small fragments; when heated more slowly it was dissipated without this decrepitation. When heated by a lens in a glass vessel placed over water, it was still dissipated, and in the first experiment no sensible product was obtained; in a second he observed, that when the heat was less powerful, the surface of the diamond became black, and was sensibly covered with a thin coating of charcoal. In a subsequent experiment, he found, that the air of the vessel in which the experiment was made was diminished in volume, to the extent of about 8 cubic inches in 60; on pouring into this residual air, lime-water, it became milky, as it would have done from exposure to air in which charcoal had burned; and by subjecting it to different trials, this milkiness was found to be owing to the presence of carbonic acid, which of course had been produced during the combustion of the diamond. The same results were obtained on heating the diamond in a glass vessel containing common air placed over quicksilver. Lavoisier drew the conclusion, that the diamond is a combustible body; and that as objects of chemistry, there exists a great analogy between it and charcoal*.

Some years afterwards, Guyton shewed that the diamond is consumed when heated with nitrate of potassa, and affords carbonic acid. This experiment was repeated with more precision by Mr Tennant. He exposed to a strong red heat for an hour and a half, in a gold tube, two grains and a half of small diamonds with a quarter of an ounce of nitrate of potassa. The salt was decomposed, and, on examining the residuum, the potassa was found to have attracted carbonic acid, while the diamonds were entirely consumed. The quantity of carbonic acid was attempted to be ascertained; by adding to the solution of the residuum in water, a solution of muriate of lime, a precipitate of carbonate of lime was formed; from this the carbonic acid was disengaged by muriatic acid, and it occupied a space equal to about 10.1 ounce measures of water. This, according to Mr Tennant's calculations, was about the quantity that ought to have been obtained from two grains and a half of charcoal combined with oxygen; and he therefore concluded that the diamond is charcoal, and differs from that substance only in its state of aggregation and its crystallized form *.

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* Mémoires de l'Acad. des Sciences, 1772, p. 500.

Guyton, some years afterwards, undertook the investigation of this subject: a diamond, (an imperfect octohedron), was placed on a small porcelain crucible elevated in a jar filled with oxygen gas ascertained to be pure, placed over mercury. The concentrated solar rays were thrown on it by a large lens; it appeared at first farinaceous, and was afterwards sensibly blackened on its surface; the appearance of combustion was extremely faint, and when it had begun did not continue, if the solar heat was withdrawn. Afterwards, when a more powerful lens was employed, the combustion was more evident; the diamond first became black and of a coally appearance; an instant after it

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* Philosophical Transactions, 1797, p. 123.

became brilliant, and at some points it appeared to boil; it gradually diminished, and the application of the solar heat was repeated at different times, until it was entirely consumed. The quantity of carbonic acid that had been formed, was ascertained by introducing a solution of barytes in water, and the unexpected result obtained, that the quantity was greater than what would have been formed by the combustion of the same weight of charcoal as of diamond. Twenty-eight parts of charcoal in burning combine with 72 of oxygen, and form 100 of carbonic acid; while the same weight of acid, according to Guyton's experiment, is formed from the combustion of 17.88 of diamond, which combine therefore with 82.12 of oxygen. Guyton concluded, therefore, that it is not by its colour, weight, hardness, transparency, and other sensible qualities, that the diamond differs from charcoal; neither does the difference depend on the state of aggregation, nor are the distinctive properties of charcoal owing to the two hundredth part of residue which it leaves in the form of ashes, or to the small quantity of hydrogen which it may contain; but to its oxidation, diamond being the simple base of which charcoal is an oxide.

The experiments of Guyton were not, however, perfectly satisfactory, particularly as to the modes of estimating the quantity of carbonic acid. Objections to this of some force have been stated by Berthollet; and he has, in particular, pointed out the source of error from Guyton estimating the quantity from the quantity of carbonate of barytes formed, by introducing barytic water to the gas after the combustion, and assuming that the proportions of this artificial carbonate of barytes would be the same as those of the natural carbonate, as ascertained by Pelletier, which, even admitting these to be correct, is not very probable [*].

Messrs Allen and Pepys, from the consideration of this uncertainty, undertook a series of experiments with the view of determining this important question [†]. The apparatus they employed consisted of a tube of platina placed across a furnace, and connected at each extremity with a mercurial gazometer; a small platina tray was placed within the tube, containing the diamond, or other substance to be operated on; and the tube being at ignition, oxygen gas, the purity of which had been carefully ascertained, was passed slowly through it, from one gazometer to the other, and was thus made to pass over the diamond a number of times. The diamond was of course consumed, and carbonic acid formed. At the end of the experiment, the whole of the gas being collected in one gazometer, the quantity of carbonic acid produced was estimated from the volume of it absorbed by lime-water; the quantity of oxygen remaining was determined by the eudiometer of sulphate of iron impregnated with nitric oxide, and of course the quantity of oxygen which had been consumed was thus discovered; and, lastly, the quantity of the diamond consumed was determined by weighing. The composition of the carbonic acid could thus be determined, either from the consumption of a given weight of oxygen, or of carbonaceous matter, in the formation of a certain quantity of it, and the one mode served as a confirmation of the other. The results by each differed very little; and in two experiments it was found, estimating from the quantity of oxygen consumed, that 100 parts of carbonic acid contain, according to the one, 28.81 of diamond; according to the other, 28.72. I shall afterwards have to state, that the proportions from charcoal and oxygen are almost precisely the same, the quantity existing in 100 parts of carbonic acid estimated from the same mode being 28.77. It may therefore be concluded from these experiments, that diamond and charcoal are essentially the same, and differ only in their aggregation and form; and the results agree nearly with those of Mr Tennant's experiments.

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[*] Mémoires de l'Institut National, t. iv. p. 288.

[†] Philosophical Transactions, 1807.

It has been stated, however, that Mr Davy, from galvanic researches on these substances, has found, that diamond contains a small quantity of oxygen, while charcoal contains a little hydrogen; and if the quantities are minute, this may be, without the results from their combustion being sensibly different; as the water formed in the combustion of the charcoal, when in small quantity, may be retained in combination with the carbonic acid gas, and may even slightly modify its volume and specific gravity.

A striking fact with regard to the oxygenizement of the diamond, is the high temperature which is requisite to it taking place. It appears, from Guyton's statement, to be charred at about the temperature of 18 or 20 of Wedgwood's scale (3417 or 3677 of Fahrenheit's), and at about 30 (4977°) it burns with a feeble flame, nor does it even in oxygen gas produce so much heat as to support its combustion. This is no doubt owing to the very strong cohesion exerted between its particles *.

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* Memoir by Guyton, Annales de Chimie, t. xxxi.; or Abstract of it in Nicholson's Journal, 4to, vol. iii. p. 298.

The appearances attending the combustion of the diamond have been observed with perhaps more accuracy by Sir George Mackenzie; and the temperature requisite has been stated by him as less high. A diamond cut and polished, when introduced into a muffle previously heated red hot, soon acquired the same redness as the muffle, but in a few minutes more became distinguished by a bright glow, and began to consume. A piece of plumbago placed beside it, exhibited a similar luminous appearance, but it began at a lower temperature. When the air was excluded from the muffle, both lost their brightness, but it returned on the admission of the air, and was much increased by blowing on them with a bellows. To ascertain at what temperature the combustion of the diamond took place, one of the pyrometrical pieces of Wedgwood was placed with it in the muffle. When both were perfectly red throughout, the pyrometer was withdrawn, and indicated 13° of Wedgwood's scale. They were replaced, and the heat increased until the glow appeared; it was kept at this as equal as possible, until the diamond was consumed; the pyrometrical piece then indicated 14°, and in another diamond the heat requisite to produce the glow and consume it was 15°. These experiments are evidently the most accurate that have been made to ascertain this point, and indeed the temperatures assigned by Guyton were rather from conjecture than experiment. Although they shew that a less elevation of temperature is requisite for the combustion of the diamond than was supposed, they still prove it to be much higher than that which is necessary for the combustion of charcoal.

Sir George Mackenzie likewise repeated and confirmed an experiment of the French Chemists, in which a piece of soft iron was converted into steel by being heated with diamond, in the same manner as it would have been by being heated in the usual manner with charcoal powder; and his experiments are more satisfactory as having been made with diamond in its purest state *.

The diamond is scarcely acted on by any other agent than by oxygen at an elevated temperature: Bergman states an experiment from which it would appear to be capable of being partially oxidized by sulphuric acid; this acid, when poured on the diamond powder, previously freed from impurities by digestion with nitro-muriatic acid, and evaporated to a small quantity, becoming black, and depositing small pellicles, which take fire on the approach of flame, and are consumed. The other acids, according to his observation, exert no sensible action on it; nor does it appear, from the experiments which he made on it with soda, (the mixture of soda and of diamond powder being exposed to a very strong heat,) that it had suffered any chemical change from the action of the alkali; for although a minute portion of earthy matter appeared to be produced, this might probably be derived from the various agents which were employed in the experiment †.

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* Nicholson's Journal, 4to, vol. iv. p. 103.

† Essays, vol. ii. p. 118.

SECT. II.

OF PLUMBAGO.

Plumbago.—The substance known in commerce by the name of black lead, and described by mineralogists under the names plumbago and graphite, is a mineral production, the nature of which was not understood until in some measure pointed out by Scheele. He shewed that, by a slow combustion, or by heating it with nitre, it is converted into carbonic acid with a small residuum of iron *. Experiments were afterwards made upon it by Pelletier, by Monge, and Vauquelin, whence it appeared to be a compound of carbon with iron, containing from 5 to 10 parts of iron in 100. Scheele observed that it required more nitre to burn it than charcoal, one part requiring 10 of the salt, whereas 5 parts are sufficient for the consumption of 1 part of charcoal ; but this was supposed to be owing to its difficult combustibility, in consequence of its aggregation and its combination with the iron, from which much of the oxygen of the nitrate of potassa was dissipated without being spent in the combustion. Guyton supposed, however, that it requires more oxygen for its saturation than charcoal does, and that a given weight of it produces a larger quantity of carbonic acid ; and hence he concluded, that it approaches nearer to the simple base, or, independent of the iron combined

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* Chemical Essays, p. 243.

with it, it may be regarded as that base in the first degree of oxidation.

This conclusion was not established by any decisive evidence ; and by the experiments of Allen and Pepys, it is now proved to be incorrect. They submitted pure plumbago to the kind of experiment already described under the history of diamond; it was consumed, leaving only a very small residuum of iron. Estimating from the quantity of it consumed, and the quantity of carbonic acid formed, it was found, that 100 parts of the acid contain 28.66 of the carbonaceous matter of plumbago ; and precisely the same proportions were found from the quantity of oxygen that had been consumed.

The carbonaceous matter existing in plumbago, it may be inferred from these experiments, is nearly the same as that composing diamond. It has been stated, however, that Mr Davy considers it as pure carbon combined with iron, while in diamond a little oxygen is contained. It approaches so far in chemical properties to diamond, as not to burn except at a very elevated temperature, and not to evolve so much caloric as is requisite to keep up the temperature necessary to its combustion, probably from its state of aggregation, or partly from its combination with the iron. This metal appears to be essential to its composition, and hence, although its general nature has been here pointed out, its chemical as well as its natural history must occupy a different place in our arrangement.

Another substance into which plumbago graduates, is that which has been named by mineralogists, Mineral Carbon, Anthracite or Incombustible Coal. It is of a black colour with some lustre, is soft, smooth and light. When exposed to heat, it does not, like the other coals, exhale any bituminous or sulphureous vapour. If exposed a long time to the fire, it consumes very slowly, with a red glow, but without flame. Hence it has received the name of incombustible coal. The greater part of it consists of carbonaceous matter, with portions of silex, argil, and oxide of iron. Guyton considered its carbonaceous matter as in an imperfect state of oxidation approaching to plumbago; and with regard to one of this variety, the blind Kilkenny coal, he remarks from Kirwan, that it is capable at ignition of decomposing 9.6 of nitrate of potassa, or nearly as much as plumbago does.

It has also been remarked, that the carbonaceous residuum, which is obtained from the decomposition of animal substances by heat in close vessels, is scarcely capable of combining with oxygen but at a high temperature; and even coal, when it has been coaked or exposed to a strong heat in close vessels, is not so easily kindled as common wood charcoal. Guyton regards them therefore as being less oxidated, whence they require a higher temperature for their combustion; and these substances, including the plumbago and anthracite, approach in this respect to the diamond, as they do also, in not evolving during their combustion a sufficient quantity of caloric to continue it. Messrs Allen and Pepys, however, have found reason to conclude, that they are essentially the same with charcoal. The anthracite, when submitted to experiment, consumed the same quantity of oxygen, and afforded the same quantity of carbonic acid, 100 grains of carbonic acid containing 28.27 of its combustible matter. Animal charcoal contains hydrogen with a portion of saline matter.

SECT. III.

OF CHARCOAL.

When vegetable matter, especially that forming the more solid parts of plants, is exposed to heat in close vessels, it is decomposed; the more volatile principles are disengaged, and there remains a black shining porous substance, composed of the matter not convertible by the high temperature to the gaseous form. This is Charcoal. It is usually obtained from the imperfect combustion of wood. The wood cut into billets, or the branches of trees from which the smaller twigs have been lopt off, being heaped together in a pyramidal pile, which is covered with earth or turf, in which a few apertures are left, heat is applied so as to kindle the internal parts of the pile. The apertures are then nearly closed, that the combustion may be carried on very slowly, and in an imperfect manner; the moisture of the wood is first dissipated; afterwards its more volatile principles, particularly its hydrogen and oxygen, pass off in combinations with part of its carbon; and the residual mass, consisting principally of carbon, which has existed as a constituent principle of the vegetable matter, is the black porous substance, common charcoal. It generally retains the figure and texture of the wood from which it has been prepared, and is obtained in largest quantity from the more dense and hard woods. This is the process which is carried on, on a large scale, to obtain charcoal as fuel. The one followed by the chemist is to put pieces of wood into a crucible, cover them with sand, and expose them to a very strong fire for an hour or two; the high temperature thus excited producing the same decomposition of the ligneous matter as the imperfect combustion in the other mode.

It is sufficiently evident, that, besides the inflammable matter which composes by far the greater part of the charcoal, it must, from the nature of the process, contain any other fixed principle which may have existed in the wood, or even any fixed substance which may have been formed in the process. It accordingly always contains a portion of saline and earthy matter, chiefly carbonates of potassa and lime, and a little oxide of iron, which remain when it is burnt; but the quantity of these is very inconsiderable, seldom amounting to a 200dth part.

Other processes have been given to obtain charcoal, in a purer state. Fixed oil, in burning, deposites a quantity of black powder, which, when it has been exposed to a red heat, without the access of air, has been supposed to afford nearly a pure charcoal: it always contains, however, a little saline matter. A similar product is obtained, by passing oil or ardent spirit through an ignited tube. Charcoal more or less pure is also separated in the decomposition of vegetable substances in the humid way. Thus, in the action of some of the acids on these substances, a brown or black colour is acquired, and a quantity of charcoal formed; and in the slow decomposition to which they are liable when immersed in water or exposed to humidity, the blackening and ultimate transition into a black mould indicate a similar result.

Lavoisier regarded charcoal, apart from the small quantity of earthy and metallic matter contained in it, as pure carbon; and the experiments of Tennant already stated, appeared to prove its identity with diamond. Guyton, on the other hand, inferred, that the inflammable matter of charcoal is an oxide of carbon. This followed from his experiments likewise already stated; charcoal, in burning, consuming less oxygen, and affording less carbonic acid than an equal weight of diamond; it must contain, therefore, less real carbon; and since its combustion affords no other sensible product than carbonic acid, the other ingredient which it evidently does contain must be one which enters into the composition of that acid, in other words must be oxygen. Carbonic Acid consists, according to Lavoisier, in round numbers of 28 charcoal and 72 oxygen; according to Guyton, of 18 pure carbon or diamond, and 82 oxygen. The difference, therefore, in the numbers of the base, is the proportion of oxygen, which, according to his opinion, must be contained in charcoal; 18 substracted from 28 give 10 as the quantity of oxygen which 28 of charcoal contain; and this gives the proportion in 100 parts in round numbers, of 64 carbon, and 36 oxygen, forming charcoal.

The experiments of Allen and Pepys already stated, have sufficiently demonstrated the fallacy of the grounds on which the conclusion of Guyton rests. With the apparatus which has been described under the history of diamond, they burnt charcoal by supplying it with oxygen gas; the charcoal having been exposed to a red heat immediately before submitting it to experiment, and being weighed as speedily as possible; indeed, while still warm, so as to guard against the fallacy which might have arisen from the hygrometric quality of charcoal, in consequence of which, it absorbs humidity from the atmosphere. The charcoal was almost entirely consumed, 4 grains leaving a residual white matter weighing only 0.02 of a grain. Calculating from the quantity of charcoal consumed, and the quantity of carbonic acid produced, it followed, that 100 grains of carbonic acid contain 28.92 of charcoal. This was confirmed by making the estimate also from the quantity of oxygen consumed, the result from this being, that in 100 grains of carbonic acid 28.77 of charcoal are contained, both agreeing almost precisely with the results from the combustion of diamond *.

From these facts the conclusion might be drawn, that the inflammable matter of charcoal is pure carbon, that it is the same as the diamond, and that the original proportions of the elements of carbonic acid, 72 of oxygen and 28 of carbonaceous base, assigned by Lavoisier, are nearly just.

There are some facts, however, from which it has been inferred, that charcoal contains hydrogen. This opinion has been supported in particular by Berthollet; the hydrogen he supposes combines during the burning of charcoal, with a portion of the oxygen forming water, which may be retained in combination with the carbonic acid, so as not to be apparent; and the proofs advanced in support of these conclusions are such as perhaps establish them to a certain extent. They are at least entitled to notice.

The existence of hydrogen in charcoal, Berthollet con-

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* Philosophical Transactions, 1807.

ceives to be established by the facts, that when it is exposed in close vessels to a strong heat, a large quantity of an inflammable gas is procured from it, which on burning affords water; and that when charcoal is burnt in oxygen gas, a little water is condensed on the sides of the receiver, as was observed in the experiments made by Lavoisier to determine the composition of carbonic acid.

These facts may however be explained, on the supposition that charcoal, which has been exposed to the atmosphere, may contain water, absorbed from the air. Of this absorption indeed there can be no doubt; charcoal after ignition increasing rapidly in weight on exposure to the air, and affording after this exposure water when urged by heat, as Allen and Pepys have shewn. To obviate this source of fallacy, and to prove that charcoal, even when calcined, contains hydrogen, Berthollet has adduced other facts apparently more conclusive.

Mr Cruickshank had observed, that the gas afforded by exposing mixtures of metallic oxides with charcoal to heat, always gave in burning a little water, which he ascribed to hydrogen derived from the charcoal. To determine this, dry charcoal, which had been obtained by distillation in iron cylinders, was introduced into a retort, and exposed to heat; much gas was produced; the portion which came over about the middle of the process being examined, was found to consist of carbonic acid and carburetted hydrogen, in the proportion of 1 of the former to 1,8 of the latter. Another portion of the same charcoal, which had been exposed to a red heat in a covered crucible, was introduced into a coated glass retort, and, on the application of heat, afforded likewise much gas;

but this gas, except at the very commencement, scarcely contained a vestige of carbonic acid. It is obvious, therefore, Mr Cruickshank observed, that the gas from the charcoal, which must have contained least humidity, contained more hydrogen and less carbon than the other, and this hydrogen therefore could not be derived from water which the charcoal might have contained. Had the hydrogen also been derived from this source, the production of carbonic acid from the union of the oxygen of the water with the charcoal might have been expected to be proportionate, which it was not *.

Berthollet himself had, at an early period, observed the production of carburetted hydrogen with little carbonic acid, from exposing charcoal to heat; and on repeating the experiment with care, he found the quantity of carbonic acid to be very small, and to be produced only at the commencement of the experiment, while the quantity of inflammable gas is considerable †.

Lavoisier had supposed, that the water which appeared in his experiments, on the combustion of charcoal in oxygen gas, owed its origin to hydrogen contained in the charcoal, and had stated the proportion of hydrogen in common charcoal at about 1.5 in 17 grains ‡; but not having observed this water, when he employed charcoal previously calcined in a strong fire, he concluded, that in this state it is free from hydrogen, and therefore that that element was not essential to it §. Berthollet remarks,

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* Nicholson's Journal, 4to, vol. v. p. 210.

† Mémoires de l'Institut National, tom. iv. p. 292.

‡ Mémoires de l'Acad. des Sciences, 1781, p. 452.

§ Ibid. 1781.

however, that even when the charcoal was well calcined, a quantity of water was deposited on the sides of the vessel at the commencement of the experiment, which was afterwards dissolved by the carbonic acid gas *. And he adds an experiment made by Hassenfratz, which he had repeated with success, that of passing oxygen gas through an ignited tube containing well calcined charcoal; at the beginning of the operation, water is deposited at the end of the tube, and the gas deposites water on cooling †.

Another proof in favour of the existence of hydrogen in charcoal, is derived from an experiment made by Mr Kirwan;—exposing to heat "a mixture of equal parts of "sulphur and pulverized charcoal, out of which its adventitious air had been as much as possible expelled by "keeping it a long time heated to redness:" sulphuretted hydrogen was procured in large quantity, either when the experiment was performed in a crucible with a cover having a small hole to allow the air to escape, or when the mixture was exposed to heat in a retort ‡.

From these facts Berthollet has drawn the conclusion, that "Charcoal is a combination of carbon and hydrogen; "it contains a small quantity of oxygen; it loses by the "action of the heat alone the oxygen, and a certain pro-"portion of the hydrogen, and of the carbon: after this "calcination, it ought to be considered as a combination "of carbon, and of a small proportion of hydrogen so re-"tained by its affinity to the carbon, that the action of

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* Mémoires de l'Institut National, tom. iv. p. 287.

† Ibid. p. 326.

‡ Philosophical Transactions, vol. lxxvi. p. 124.

" heat cannot separate it, at least unless oxygen be intro-" duced *." The diamond he regards as pure carbon; and it is the want of hydrogen, in Berthollet's opinion, that renders it less combustible than charcoal, or causes it to require a more elevated temperature to burn.

Clement and Desormes brought forward some experiments † which are in contradiction with the preceding results, and which they consider as sufficient to prove that no sensible proportion of hydrogen is contained in well calcined charcoal. They observe, that although charcoal, in its usual state of preparation, gives out a quantity of an inflammable gas by exposure to heat; yet, when urged by a strong heat, this diminishes, and at length ceases; nor after a certain period is any gas obtained from it in close vessels by the most intense heat. This obviates, therefore, the conclusion drawn from the production of such a gas from charcoal; and when it is urged by a strong fire till it has ceased to afford any elastic fluid, they regard it as free from hydrogen. They state, too, what is indeed sufficiently certain, that when charcoal is exposed to the atmosphere, it absorbs humidity, and afterwards gives water in its combustion. But when removed from a furnace, and placed in an apparatus, in which, without previous exposure to the air, it can be made to burn, no sensible portion of water, they affirm, is produced. This they ascertained by placing charcoal in this state in a tube across a furnace, one end of it being connected with a tube containing muriate of lime, a salt which has a strong affinity

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* Mémoires de l'Institut National, tom. iv. p. 315.

† Philosophical Magazine, vol. xiii. p. 67. 158.

to water, and to the extremity of which was attached a prepared bladder containing oxygen. The other end of the tube containing the charcoal was connected with a tube likewise containing muriate of lime, and having an empty prepared bladder attached to it. The charcoal being sufficiently heated, the oxygen gas was made to pass over it: the muriate of lime over which it *previously* was transmitted, increased in weight 0.13 grammes from the deposition of its water; but the muriate of lime over which the product of the combustion passed did not increase more than 0.02 grammes,—a proof that no water had been produced in the combustion, or at most, such a quantity as not to give a quantity of hydrogen in charcoal more than $\frac{1}{1300}$, that is, a quantity scarcely appreciable; whereas Berthollet supposed the quantity of hydrogen in charcoal to be about 7.90 in 100. They have also stated, that the quantities of carbonic acid produced in the combustion of different varieties of charcoal, plumbago and anthracite, are from equal weights the same, and that these substances in burning require nearly the same quantity of oxygen. Several of these facts are confirmed by Allen and Pepys. They observed in particular, that in burning charcoal, by supplying it, when ignited, with a stream of oxygen gas, there was no appearance of mixture.

With regard to the production of Sulphuretted hydrogen, from causing sulphur and charcoal to act on each other at a red heat, Clement and Desormes have affirmed, that though a little gas is obtained, it is not sulphuretted hydrogen, and that the liquid which is the principal product is a compound of sulphur and charcoal. Under the history of sulphur, it has been stated, however, that there is every reason to conclude, that this substance is a compound of sulphur and hydrogen: and with regard to the gaseous product, Berthollet has repeated the experiment of Kirwan in such a manner as appears to prove the existence of hydrogen in the best calcined charcoal. 30 grammes (463.3 grains) of charcoal immediately removed from a large fire in which it had been strongly calcined, were mixed with 20 grammes (308.8 grains) of sulphur in an earthen-ware retort, and heat applied; above 40 cubic inches of gas were disengaged and collected, which was ascertained to be sulphuretted hydrogen by its inflammation, and by the effect of its solution in water on the metallic salts. "If the calcined charcoal," says Berthollet, "had not given sulphuretted hydrogen, no conclusion could be drawn from thence against the existence of the hydrogen, because by its proportion being too much diminished, it might be retained by a force so powerful that the sulphur, the volatility of which would occasion its speedy separation, might not be able to disengage any more: but since, notwithstanding this circumstance, it had been obtained from charcoal strongly calcined, and by a heat much lower than that which it had before supported, and since there can be no doubt of the existence of hydrogen in the sulphuretted hydrogen, this fact is a positive proof that the charcoal itself, after having been submitted to a strong calcination, contains hydrogen *."

From these statements, in some measure at variance as to point of fact, it is not easy to draw a certain conclusion. The production of an elastic fluid from charcoal, urged by

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* Chemical Statics, vol. ii, p. 37.

a strong heat, is not conclusive in proof of the presence of hydrogen; for, independent of the circumstance that it may be owing to the charcoal being not perfectly calcined, there is a fallacy from the possibility of the presence of water which charcoal imbibes so quickly from the atmosphere; and the reasoning of Cruickshank and Berthollet, that did the production of the elastic fluid depend on this water, it ought to consist in part at least of carbonic acid, is not perfectly correct. It is perfectly possible, that, while the hydrogen of the water forms with the carbon, carburetted hydrogen, the oxygen may form not carbonic acid, but carbonic oxide; or, what is equally probable, the oxygen and hydrogen of the water may enter into simultaneous combination with the carbon, and form a ternary elastic compound; and there is every reason to believe, indeed, that the gas given out by charcoal, when urged by a strong heat, is actually of this kind.

The production of sulphuretted hydrogen, when charcoal and sulphur are exposed to a strong heat, is however a much more conclusive proof; for, as has been already stated, this product is obtained when charcoal is used thoroughly calcined, and removed at once from the fire, without remaining exposed to the air, in which case the presence of water cannot be suspected. The experiment of Berthollet on this point, above stated, appears unexceptionable; and Berthollet *junior* has stated, that a similar product is obtained when charcoal was used which had been kept for an hour in the heat of a forge capable of softening a Hessian crucible, and which by that temperature had lost more than one-fourth of its weight. It obliges us to admit, as he remarks, that hydrogen exists in charcoal which has been exposed to the most powerful heat we can produce *; unless indeed we suppose, what is not probable, that the whole of the hydrogen of the large quantity of sulphuretted hydrogen obtained had been derived from the sulphur.

The production of water in the combustion of charcoal is a more doubtful proof, since the fact is denied that any water is deposited. But if it even be admitted that none is deposited, this does not disprove the existence of at least a certain portion of hydrogen in charcoal, since, if not considerable, the water formed might be retained in combination by the carbonic acid gas.

There are even facts which render it probable that a little oxygen also may exist in charcoal. It has been observed, in particular, what is a very striking fact, in the greater number of the experiments made on the combustion of the diamond, that its surface, at a certain stage of temperature, became black or sensibly charred; and Lavoisier even remarked in some of his experiments, that a black powder was formed on its surface, which was easily removed, and which soiled the fingers †. " Cinq de ces " diamans se sont trouvés après l'experience d'un noir mat " et velouté, precisement comme s'ils avoient été enduits " de noire de fumée à la flamme d'une lampe; ils noircis- " soient les doigts et le papier, precisement comme auroit " fait une substance charbonneuse ou du noir de fumée."

The most probable conclusion, indeed, from theory, would be, that charcoal may contain minute quantities

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* Mémoires de la Société d'Arcueil, p. 322.

† Mémoires de l'Acad. des Sciences, 1772, 414. 418.

both of oxygen and hydrogen. When principles disposed to assume the elastic state are disengaged by heat, from their combination with a substance which is comparatively fixed, in proportion as the decomposition proceeds; the former will be retained with a stronger force, the affinity of the fixed substance towards them being augmented by the increase in its relative quantity. If a vegetable substance, composed of carbon, hydrogen, and oxygen, be exposed to heat, this law may be expected to be observed; and although, by the elevated temperature, the greater part of the oxygen and hydrogen may be expelled, carrying with them portions of carbon, it seems sufficiently probable that the last portions of them will be obstinately retained, and will thus form with the carbon a ternary combination,—that charcoal, therefore, will consist of the pure carbonaceous base, with small proportions of oxygen and hydrogen.

The principal or rather the only difficulty in the conclusion, that hydrogen exists in charcoal, is derived from the experiments, which prove, that the same quantity of carbonic acid is produced in burning from charcoal as from diamond. Perhaps, however, this only proves that the quantity must be small; for if not considerable, it is possible that this result might be obtained: the water formed from the hydrogen of the charcoal might exist in the elastic form combined with the carbonic acid, and add so far to its volume as that this should appear equal to the volume of carbonic acid produced from the combustion of the same weight of diamond, though this contained no hydrogen. And as hydrogen combines with a larger proportion of oxygen than carbon, this might give rise to the apparent equality in the consumption of charcoal and diamond, though the former contained a small quantity of oxygen as well as of hydrogen.

I have already stated, that from galvanic researches on these bodies, it is inferred that diamond contains a little oxygen, and charcoal a small portion of hydrogen.

WOOD-CHARCOAL, in its usual state of preparation, is a solid, extremely porous substance, of a deep black colour, brittle, and easily reduced to powder; it is perfectly tasteless and inodorous. When obtained from the decomposition or imperfect combustion of some other vegetable substances, it is in this state of a black spongy powder.

Charcoal is altogether infusible by heat; nor in close vessels is its texture, or any of its physical properties changed, though it is urged by the most intense fire. When the heat is at first applied, so as to bring it to ignition, a quantity of gas is disengaged, and the production of this continues for some time. It consists of carbonic acid, and of a variety of carburetted hydrogen; the first is always in inconsiderable proportion, and is disengaged principally in the beginning of the experiment. At this stage, according to Berthollet, it amounts to about one-sixth of the volume of the whole gas; and in the latter stages to one-tenth. According to Mr Cruickshank's experiments, its proportion is still less; and towards the end of the experiment, it is scarcely in any appreciable quantity. The inflammable gas is in large quantity. Berthollet, in experiments made at an early period, obtained 720 cubic inches from one ounce of charcoal *; and the char-

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* Mémoires de l'Acad. des Sciences, 1781, p. 228.

coal lost nearly one-fourth of its weight. He found considerable differences, as is stated in a subsequent memoir *, in the carburetted hydrogen obtained in different experiments ; and these differences were also observable, when a well prepared charcoal was employed, in different stages of the process. The following table, which he has since given †, shews these differences, by indicating the quantities of carbonic acid obtained from a given quantity of the gas collected in ten successive portions :

1 . 100	of carburetted hydrogen gas,	35.5 carbonic acid.
2 . 100	- - -	39.5
3 . 100	- - -	35
4 . 100	- - -	10
5 . 100	- - -	10
6 . 100	- - -	17.5
7 . 100	- - -	12.5
8 . 100	- - -	10
9 . 100	- - -	10
10 . 100	- - -	10

The proportions of oxygen which these portions of gas required for saturation, were somewhat different; the medium was about 60 parts of oxygen to 100 of the gas. He observed that in the beginning of the operation, a little water was disengaged, although the charcoal employed had been perfectly dry. Clement and Desormes found, that when common charcoal was exposed to a strong heat, in an earthen retort, or iron tube, for two hours, it gave out

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[*] Mémoires de l'Acad. des Sciences, 1785.

[†] Mémoires de l'Institut National, t. iv. p. 292.

gas only the first hour; during the second it yielded none *.

This production of an aëriform fluid by heat from common charcoal, may probably in part be owing, as has been already explained, to the decomposition of the water it contains,—the elements of which enter chiefly into a ternary combination with part of its carbon, and form the inflammable gas; and partly perhaps to portions of the hydrogen and oxygen of the original vegetable matter still remaining in the charcoal, prepared in the usual mode, and being disengaged in combination with carbon at a high temperature. It does not appear, that by this process the physical or chemical properties of the charcoal are very materially changed. It is rendered, however, by this thorough calcination, a better conductor of galvanism.

Charcoal is altogether insoluble in water; nor at a moderate temperature is it in any way affected by it. Wood, therefore, which has been charred, is preserved a long time unchanged, though exposed to humidity, or immersed in water; and solid vegetable matter, which, under exposure to water, has suffered spontaneous decomposition, is converted into a black substance, consisting principally of charcoal, beyond which the decomposition does not proceed. Charcoal when newly calcined absorbs humidity from the atmosphere very quickly, and to such an extent as to be sensibly increased in weight. According to Clement and Desormes, a piece of charcoal weighing 4 grammes (61.7 grains), on exposure even to a dry atmosphere, increased in weight 0.2 of a gramme (3 grains) †. Messrs

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* Annales de Chimie, t. xxxix. p. 29.

† Ibid. t. xlii. p. 123.

Allen and Pepys found, that different kinds of charcoal increased in weight from a week's exposure, after they had been thoroughly ignited, from 10 to 18 *per cent.*; and as they increased little in weight when exposed to confined air, the increase must be ascribed to absorption of water from the air. They also found, that the greatest increase took place in the first hour or two after exposure, and arrived at its maximum in 24 hours. By exposure to heat, this water is expelled, partly undecomposed, and partly in a state of new combination, from the union of a portion of its elements with the charcoal. At the temperature of ignition, water is decomposed by charcoal; carbonic acid gas, and an inflammable gas, which has been regarded as a compound of carbon and hydrogen, and which is afterwards to be noticed, being formed.

A property of which charcoal is very eminently possessed, and which may be regarded as a singular one, is that of absorbing, even when cold, aëriform fluids, and condensing them in its pores, without forming with them, at the temperature at which this happens, any intimate chemical combination, or suffering any change in its properties. This property is exhibited, by removing a piece of charcoal, when red-hot, into a tube filled with quicksilver; if when it has cooled in this situation, a quantity of aëriform fluid be admitted into the tube, an absorption of it takes place many times the bulk of the charcoal.

This property had been observed and made the subject of experiment by Scheele, Priestley, and Fontana; but it has been examined with more attention by Morozzo and Rouppe. Morozzo employed pieces of charcoal of a determinate size (1 inch in length, and 8 lines in diameter), which, after being ignited, he plunged into mercury, and introduced into a glass tube, of an inch in diameter, and 12 inches long, placed in the mercury, and filled with the gas designed to be submitted to trial. A piece of charcoal of this size being introduced into the tube, filled, for example, with atmospheric air, the quicksilver rose in the tube to the height of 3 inches 6 lines. The following table shews the relative proportions of the different gases that were absorbed.

Gases absorbed.	Inches.	Lines.
Atmospheric air, - -	3	6
Carbonic acid gas, - -	11	
Nitric oxide gas, - -	6	10
Hydrogen gas, - -	2	1
Oxygen gas, - -	2	2
Ammonia, - - -	11	
Muriatic acid gas, - -	11	
Sulphuretted hydrogen gas, -	11	
Sulphurous acid gas, - -	5	6 *

The experiments of Morozzo were repeated and varied by Rouppe and Van Noorden, and with similar results. They employed an apparatus, in which the charcoal, in a state of ignition, was allowed to cool completely without exposure to the air, and without being plunged in quicksilver; and, when fully cold, the air was exposed to it, the absorption being indicated by the rise of the water, in which the tube containing the air stood, and by which of course the pressure of the atmosphere was less counteracted than in the experiments where quicksilver was employed. The pieces of charcoal

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* Journal de Physique, 1783.

were about 16 or 17 inches in volume. The quantities of the airs absorbed were in the following proportions:

Atmospheric air, 36 inches immediately, and in 4 or 5 hours, 48.
Oxygen gas, 30 inches immediately, and slowly to 46.
Nitrogen gas, 27 inches immediately.
Nitric oxide gas, slowly to the extent of 136 inches.
Hydrogen gas, from 29 to 31 inches immediately.
Carbonic acid gas, 230 inches immediately *.

Morozzo resumed his experiments, with an apparatus in which the charcoal was exposed, as it had been in those of Rouppe, to the gases, without having been immersed in quicksilver; which, from its interstices being filled with the fluid, it might be supposed would diminish its absorbing power. It was introduced therefore into a closed cavity, which communicated by a stop-cock with a glass tube placed in quicksilver, and containing the gas to be submitted to experiment. The results differ from the former with regard to some of the gases, and agree as to others. Atmospheric air suffered a diminution of volume of about one-third, instead of only about one-fourth, the result given in the first experiments. Oxygen presented a deviation still more striking, the absorption, instead of being only 2 inches out of 12, amounting to 12 out of 18, in 4 hours; in 48 hours to 13 inches 6 lines; in 3 days, 14 inches 5 lines; and in 8 days being total. The absorption of hydrogen and of carbonic acid gases, appeared to be the same in the second as in the first experiments. That of nitrogen gas, which had not been formerly tried, was found to amount to 6 inches in a tube 18 inches long;

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* Annales de Chimie, t. xxxii. p. 1.

on referring to the standard in the above table, it would be equal to 4[*]. His experiments appear to have been made on the charcoal before it had cooled much, in which respect they differ from those of Rouppe; and this method is undoubtedly less accurate, as at that high temperature chemical action may take place.

Several interesting facts have been ascertained with regard to this absorption or condensation of elastic fluids by charcoal, particularly by Rouppe. It had been supposed, that the elastic fluids absorbed by the charcoal suffer some changes besides condensation. According to his experiments they do not; and when they have appeared to do so, or have been obtained from the charcoal in a different state from that in which they were absorbed, he supposes it owing to the charcoal having been previously exposed to another gas, or to atmospheric air, by which an intermixture would be occasioned. Sometimes also it may have been owing to incandescent charcoal having been employed. Sennebier stated some experiments in which atmospheric air appeared to be decomposed in this absorption, its oxygen being absorbed in larger proportion than the nitrogen[†]; but the injury the air appeared to sustain, was probably rather owing to the action of the water over which it was confined; and according to Rouppe, atmospheric air is absorbed unaltered. The greater part of the absorbed gas is again expelled by a heat inferior to that of boiling water, and likewise to a certain extent by immersion in water. Neither does the charcoal appear to be materially changed in its properties, and by exposing it again to heat, it can be employed with the same effect in the experiment. The pieces of charcoal which have been employed in the experiment, Morozzo found increased a little in weight, generally from half a grain to two grains. The absorption Rouppe found, as might indeed be expected, is increased by cold, which will so far diminish the elasticity of the gas, the antagonist to the absorbing power of the charcoal.

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[*] Nicholson's Journal, vol. ix. p. 255.; vol. x. p. 12.

[†] Annales de Chimie, tom. iv. p. 261.

There are few phenomena that can be regarded as more singular than this. A large quantity of elastic fluid is condensed by the charcoal; there must therefore have been exerted a powerful attraction, by which the elasticity of the gas has been overcome. Yet this attraction can scarcely be denominated chemical, since the gas appears to exist merely condensed in the pores of the charcoal, its properties, as well as those of the charcoal, remaining unchanged; gases too are thus condensed, to which, under any circumstances with which we are acquainted, charcoal does not exert any chemical attraction, and they are reproduced pure by a slight elevation of temperature. So far as has been discovered, no substance exerts a similar power.

An interesting application may be made of this property. The gases which are absorbed suffering so great a condensation, two gases introduced at once into the pores of the charcoal in this condensed state, may perhaps be made to combine. The obstacle to the exertion of the mutual attraction of gases is the elasticity of each; this is counteracted by this absorption, without at the same time any new affinity being exerted: hence, if a piece of charcoal be exposed to a mixture of gases, or first to one and afterwards to another, the quantities of condensed gas which will be contained in it may be capable of exerting any mutual affinity which exists between them. There is accordingly reason to believe, from some experiments by Rouppe, that such combinations may be effected. Charcoal which had been previously exposed to hydrogen gas, on being exposed to atmospheric air, did not absorb it unchanged as pure charcoal would have done, but absorbed chiefly its oxygen, and a few drops of water appeared. Exposed to pure oxygen, the absorption was more rapid and considerable; and, by applying a thermometer to the charcoal, it was raised during the experiment from 52° to 100°. Charcoal, charged in like manner with hydrogen, absorbed and decomposed nitric oxide gas, water being formed and nitrogen gas being the residuum; charged with oxygen and exposed to hydrogen, it is stated there was also a formation of watery vapour; or, placed in nitric oxide gas, it caused a rapid and considerable absorption; charged with nitrogen, and exposed to atmospheric air, it is said to have deprived it almost entirely of its oxygen *. The subject deserves to be prosecuted; and if strong mechanical pressure were applied at the same time, it is probable such combinations might be diversified, and carried to a greater extent.

As charcoal absorbs these aëriform fluids, so they even at common temperatures appear to be capable of dissolving a small portion of it. Oxygen gas, when brought in contact with humid vegetable matter, abstracts carbon from it, forming carbonic acid. From the experiments of Hu-

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* Annales de Chimie, tom. xxxii. p. 16.

ber on Germination, it appears that hydrogen has the same effect; hydrogen gas exposed to seeds moistened becoming impregnated with carbon, so as afterwards to afford carbonic acid when detonated with oxygen.

At an elevated temperature charcoal enters into combination with oxygen, the combination being attended with combustion. Charcoal ignited burns in atmospheric air without flame, but with a red glow, and the emission of much heat: the compound it forms being gaseous, it appears to be entirely consumed, the residual ashes not amounting to a 200dth part of the charcoal. In oxygen gas its combustion is more vivid, a white light with scintillations accompanying it. The product of the combustion of charcoal is, as has been already stated, carbonic acid, 28 of charcoal combining with 72 of oxygen.

In consequence of its affinity to oxygen, charcoal abstracts that principle, both in the humid way and by the application of heat, from many of its combinations, especially from the acids, and the metallic oxides and salts.

Charcoal at an elevated temperature is likewise capable of combining with hydrogen. This combination was obtained by Dr Priestley, by concentrating the solar rays by a lens on a fragment of charcoal placed in a vessel of hydrogen gas. The compound remains in the elastic form, with an increased specific gravity. The same compound was obtained by Clement and Desormes, by passing hydrogen gas repeatedly through an ignited tube containing charcoal. With nitrogen, charcoal contracts no union. It combines with sulphur. It has already been stated, that the substance considered as a compound of charcoal and sulphur, by Clement and Desormes, and named by them carburetted sulphur, appears to contain no charcoal, but to be a compound of sulphur with hydrogen. Berthollet *junior*, however, in his experiments on this subject, found, that on passing sulphur over ignited charcoal, so as to form this product, the charcoal at the end of the operation retained a little sulphur in combination. This sulphur was not expelled by heat, but it could be abstracted by the alkalis or by combustion. It appears too that a ternary compound of carbon, hydrogen and sulphur can be formed; a gas of this kind being extricated when a great excess of sulphur is passed over charcoal, at a very high temperature. This gas is only partially soluble in water; and it requires for its combustion an equal volume of oxygen *.

Charcoal combines with several of the metals. These combinations are to be afterwards noticed.

The action of the fixed alkalis, potassa and soda, on charcoal, is somewhat doubtful. If exposed to heat, mixed with a portion of either, a substance is obtained, which, when dissolved in water, gives a liquor of a dark brown colour, which passes through the filter; and by boiling a solution of potassa on charcoal powder, a similar liquor is formed. Yet this has been supposed to arise from the impurities, or the portion of hydrogen present in charcoal not thoroughly calcined, though perhaps without sufficient reason. Mrs Fulhame found this solution to have the effect of charcoal in reducing metallic solutions †.

A number of the acids are decomposed by charcoal, their oxygen being attracted by it. Nitric, or rather nitrous acid, suffers this decomposition from charcoal powder with great rapidity, its oxygen being abstracted partially or completely, and nitrogen, nitric oxide, and carbonic acid gases being disengaged : if the acid be concentrated, and the charcoal perfectly dry, and somewhat warm, the oxygenizement of the charcoal is so rapid as to be attended with combustion. With the nitrates at a high temperature, charcoal suffers deflagration. Sulphuric and phosphoric acids are likewise de-oxidated by its action, either at a low or at a high temperature.

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* Mémoires de la Société d'Arcueil, t. i. p. 321. 326.

† Essay on Combustion, p. 126.

A singular property possessed by charcoal, and depending on some chemical agency it exerts, still remains to be mentioned,—that of removing the taste, odour, and colour of many vegetable and animal substances, especially those of a mucilaginous, oily or extractive nature. For the first accurate experiments of this kind, we are indebted to Mr Lowitz of Petersburgh. They are extremely numerous ; a few of the principal facts, therefore, only can be stated, to exemplify this singular quality.

Common vinegar on being boiled with charcoal powder becomes perfectly limpid. Acid of tartar, when of a brown colour, is rendered colourless by its solution in water being boiled in the same manner ; as are also solutions of crude tartar, crude nitre, and other salts, which, in their usual state of preparation, are of a yellow or brownish tinge, so that crystals are afforded perfectly white, and frequently of a different figure from what the same salts usually assume. The impure carbonate of ammonia, which is obtained by sublimation from bones, is rendered perfectly white, and is deprived of its fœtid odour by sublimation with an equal weight of charcoal powder. Malt spirit by distillation from charcoal is freed from its disagreeable flavour, though if too large a proportion of charcoal has been used, part of the spirit appears to be decomposed, as is also the case in distilling vinegar with a similar addition. By mere maceration, in the proportion of about two ounces to eight or ten pounds, the flavour of the spirit is in eight or ten days improved. Water which, from having been long kept in wooden vessels, has acquired an offensive smell, is quite deprived of it by filtration through charcoal powder, or even by agitation with it for a few minutes, especially when a few drops of sulphuric acid have also been added,—a process which may be employed to correct the fœtor water acquires in long voyages *. The fœtor even of putrid animal matter is in a great measure removed by the admixture of charcoal. Resinous substances and balsams dissolved in alkohol, and subjected to the action of charcoal, either by agitation with it, or filtration through it, are deprived of their colour, but not of their peculiar smell. The smell also of essential oils, either pure or when they are dissolved in spirit, is not affected by a similar process; that of empyreumatic oils, however, in a similar solution, as well as their colour, ate completely destroyed. Distilled waters lose their odour, wines be-

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* It appears that this has been carried into execution; casks thoroughly charred on the internal surface having been found to preserve water perfectly uncorrupted. This mode is even preferable to that of adding charcoal powder, both as the water is preserved clear, and the extractive matter of the wood is not dissolved by it *.

* Nicholson's Journal, vol. xv. p. 226.

come colourless, as do a number of the vegetable tinctures, and of the lakes and pigments, as litmus, indigo, &c. when dissolved in water; and the gum-resins, opium, assafœtida, &c. suspended in water, are deprived of their peculiar odours. The astringency of vegetables appears to be impaired or destroyed by the infusions of those which possess it being digested with a large quantity of charcoal *.

These experiments have, to a certain extent, been confirmed by other chemists, particularly by Brugnatelli, Westrumb, Gadolin, and Kels †. I have made the experiment of the purification of the impure carbonate of ammonia above stated, and found it perfectly to succeed. Some chemists, however, Göttling, Hahneman and others, have failed more or less in these experiments, probably from the proper preparation and the necessary proportions of the charcoal not having been attended to. Mr Lowitz has given on this subject several necessary rules. The charcoal must have been well burnt, and brought to a red heat before it is used; it should be in fine powder, and if not immediately used, carefully secluded from the air; and the requisite proportion must be ascertained by repeated experiments on a small scale, as, if too little is employed, the effect will not be obtained; while, in some cases, if there is an over-proportion, part of the substance designed to be purified is decomposed ‡. The same charcoal may be repeatedly used, by keeping it for some time in a state of ignition after it has been employed.

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* Crell's Chemical Journal, vol. ii. p. 165. 237.

† Ibid. p. 183.; vol. iii. p. 270. ‡ Vol. ii. p. 270.

No satisfactory theory has been given of the action of charcoal in producing these effects. It is evidently not mechanical, arising from its imbibing the matter it abstracts, but must be chemical. This is established not only by the nature of the changes themselves, but by the decompositions it produces when it is used in large proportion.

The uses of charcoal are extensive. As common fuel it affords a strong and steady heat without smoke, and hence, in chemical experiments, and in certain arts, as in dyeing, or in operations on the metals, it is preferred to coal; in metallurgic processes, too, where it is employed to reduce the metallic oxides to the metallic state, it is more manageable, and affords perhaps a purer metal, though in this country, from the comparative scarcity of wood, coaked coal is generally substituted for it. By cementation with charcoal, iron is converted into steel. It is used in the manufacture of gunpowder; in its finer state of aggregation, as under the form of what are named ivory-black, lamp-black, &c. it is the basis of several black paints; with fat oils, mixed with resinous matter to give due consistence, it forms the composition of printing ink; it is used, as has been stated, in various cases, from its property of destroying colour and odour, and of resisting putrefaction; and some applications of it have been already taken notice of, from its imperfect conducting power with regard to heat.

SECT. IV.

OF CARBONIC ACID.

ALTHOUGH the formation and disengagement of this acid in chemical processes, must have occasionally attracted the notice of chemists, no just idea was formed of its mode of existence, its nature, or properties, prior to its discovery by Dr Black. The accumulation of a noxious vapour in caverns and mines was indeed frequently observed, as well as the production of a similar vapour in fermentation and combustion ; and this appears to have been regarded as a species of air by Van Helmont, Boyle, and Hales. The existence of such an aëriform or elastic fluid in mineral waters was also noticed by Hoffman, Venel, and Brownrigg. But it was not distinguished from other aëriform fluids : its characteristic qualities were not discovered ; nor its combinations, or its influence in chemical phenomena traced. These were the discoveries of Black ; important not only in themselves, but as having laid the foundation of Pneumatic Chemistry *. Bewly and Bergman observed its acid powers, which are so weak as not to be very apparent. Cavendish and Priestley investigated several of its properties : And the fact having been observed by Dr Black, and ascertained by direct experiment, that it is produced in the combustion of coal

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* They were first published in his Inaugural Dissertation, *De Magnesia Alba*, and afterwards in the 2d volume of the Edinburgh Physical and Literary Essays.

and charcoal, Lavoisier, in consequence of his theoretical views, was led to regard it as a compound of the inflammable matter of these substances with oxygen,—an opinion, the truth of which he established by his experiments on the combustion of charcoal in pure oxygen gas. It received from Dr Black the name of Fixed Air, from other chemists successively the appellations of Aërial Acid, Mephitic Acid, and Cretaceous Acid ; terms which have given place to the preferable name of Carbonic Acid.

Carbonic Acid Gas may be said to exist in nature in an uncombined state. It is often accumulated in caverns and mines, and forms that species of noxious elastic fluid which has been named by the miners Choak Damp. The Grotto del Cano, near Naples, is celebrated for its production of it. In some mineral waters it is so abundant, as to be disengaged when they issue from the spring ; and a small portion of it, as has already been stated, exists in atmospheric air.

In a state of combination it is extremely abundant. All the varieties of Limestone, Marble, Chalk, and Marl, and all the Calcareous Crystals as they are named, are compounds of it with lime. It exists in nature combined with some of the other earths, particularly with barytes and strontites ; and is found as a constituent principle of a number of metallic ores.

It is generally obtained from any of the native carbonates of lime, as marble or chalk. If these be exposed to a strong red heat, the carbonic acid is dislodged from its combination with the lime, and assumes the elastic form ; but as the application of this high temperature is attended with some difficulty, an easier process is to separate it from its combination, by the exertion of a superior affinity. A quantity of pounded marble or chalk is put into a flask, to which a bent tube is adapted, and sulphuric or muriatic acid diluted with water being poured upon it, a rapid effervescence takes place, from the disengagement of the carbonic acid gas. It may be received over mercury or water; by the latter fluid, it is absorbed, but not immediately, in large quantity, at least where agitation is not employed, and it is more convenient operating with it than with quicksilver. In other processes in which carbonic acid is formed, as in fermentation or combustion, it is either not perfectly pure, or not disengaged in sufficient quantity, in a short time; and hence they are seldom had recourse to, to obtain it.

The production of it, however, by the direct combination of its constituent principles, in other words, by the combustion of charcoal, though not a usual mode of obtaining it, is an important experiment, as determining its composition, and the proportions of its parts. It was accordingly performed by Lavoisier with much care. A piece of charcoal, of a determinate weight, was placed in pure oxygen gas, over quicksilver, and a very small bit of phosphorus being attached to the charcoal, it was kindled by a bent iron wire, heated red hot; when the combustion had ceased, and the apparatus become cold, solution of potassa was introduced, by which the carbonic acid that had been formed was absorbed; the diminution of volume in the oxygen gas was thus discovered, and of course the quantity of it which had entered into the composition of the carbonic acid; and the remaining charcoal being likewise weighed, the loss of weight gave the quantity of it which had combined with the portion of oxygen spent in the combustion.

The results of the experiments, however, were not uniform, and there was found a difficulty in determining the proportions, principally from the formation of a portion of water. Thus, in the first experiment, the quantity of oxygen employed in the experiment was 202.35 cubic inches, which, on the assumption that a cubic inch weighs 0.47317 grain, amounts to - 95.74595 grains.
The charcoal consumed was equal to 17.20000

The whole amounted therefore to 112.94595 grains.
But the weights of the remaining oxygen, and of the carbonic acid formed, amounted only to - - 101.9352
Hence a deficit of - - 11.01075

The same loss of weight was observed in other experiments, and was ascribed by Lavoisier to the formation of water from hydrogen existing in the charcoal, and which had either been dissolved by the residual gases giving them a greater specific gravity than was calculated on, or had been deposited. And accordingly in these experiments it is stated, " that a few drops of water were collected on the surface of the quicksilver, and even on the sides of the vessel." The 11 grains of deficit were therefore assumed to have been water, and as these 11 grains contain 1.4463 of hydrogen, this quantity of this element must be contained in 17.2 of common charcoal. With these corrections the proportions of charcoal and oxygen in carbonic acid are 23.45 of the former, 76.55 of the latter *. As determined by another experiment of a similar kind, which Lavoisier selects as having been made under the most favourable circumstances, and therefore most to be relied on, they are stated at 28.399 charcoal, 71.601 oxygen †.

It was next attempted to avoid the source of fallacy from the formation of water, by operating on charcoal thoroughly calcined by exposure for two hours in a covered crucible to a very strong fire, and which was presumed to contain no hydrogen; though even with this there was a source of error, from its absorbing both air and humidity with great rapidity. The experiment of this kind, which was regarded as the most accurate of a number made, gave the result that carbonic acid consists of charcoal 28.888, oxygen 71.11 ‡.

Experiments were also made on the formation of carbonic acid in the combustion of wax, which, from the products it affords in burning, is proved to be a compound of carbon and hydrogen. The proportions of the acid were from these calculated in one experiment to be 69.675 oxygen, and 30.325 carbon; in another 71.78, and 28.22; results on which less dependence can be placed than on the preceding, as attained by a more complicated method. The same objection applies to some others, in which charcoal was combined with oxygen, not immediately, but indirectly from the decomposition of water or of metallic oxides.

The average of all these experiments makes the pro-

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* Mémoires de l'Acad. des Sciences, 1781, p. 452.

† Ibid. 453.

‡ Ibid. 454.

portions between 28 and 29 of charcoal, and 72 and 71 of oxygen *.

The experiment was likewise made by Clement and Desormes, apparently with considerable care, on charcoal thoroughly calcined, and kindled by a lens in oxygen gas, obtained from oxymuriate of potassa and previously exposed to potassa. They fix the proportions at 71.4 oxygen, and 28.6 pure charcoal †.

I have already stated, that this subject has more lately engaged the attention of Messrs Allen and Pepys, and that they had undertaken the investigation of it with the view of removing the doubts existing with regard to it from the experiments of Guyton, which appeared to prove that charcoal is not the base of carbonic acid; that diamond is this base, or pure carbon; and that from the supposed fact of the diamond consuming more oxygen than charcoal, 100 parts of carbonic acid consist of 17.88 of carbon, and 82.12 of oxygen. The results I have also stated. They employed every precaution to avoid any source of error; they found, that the diamond, and charcoal perfectly calcined, consume almost precisely the same quantities of oxygen in their combustion, and afford the same quantity of carbonic acid, and, as the average result of

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* All the above numbers were altered a little in a subsequent edition of his Memoirs by Lavoisier, in consequence of his finding the specific gravity of the oxygen gas to be somewhat greater than he had stated. But the alterations are not important, especially where the result is only an approximation, and the average may still be regarded as he states it in his Elements, 28 to 72.

† Annales de Chimie, t. xxxix. p. 42.

their experiments, they state the proportions of the elements of carbonic acid at 28.6 carbon, and 71.4 of oxygen, which agree with those of Lavoisier, and also, as they have shewn, with those which may be inferred from the experiments of Mr Tennant on the combustion of the diamond *.

If charcoal contain hydrogen, this must be the source of some fallacy in the above estimate, since it must combine with part of the oxygen consumed to form water. And accordingly Berthollet, from the quantity of hydrogen which he supposes to exist in charcoal, gives, as an approximation to the composition of carbonic acid in its usual state, the following proportions deduced from the experiments of Lavoisier, and, as he expresses it, from the comparison of many results: In 100 cubic inches, 84 cubic inches or 43 grains of oxygen, 16 grains of carbon, and 10 grains of combined water †. But there is not much probability in the supposition that so large a quantity of water can exist combined in carbonic acid; the proportion of hydrogen in charcoal is probably over-rated, and the estimate of Lavoisier, confirmed as it is by the other authorities which have been stated, may still be regarded as affording the nearest approximation.

In the conversion of oxygen gas into carbonic acid gas, whether by combination with charcoal or with pure carbon, it has been supposed to suffer a perceptible condensation, the amount of which, however, is very variously stated. Crawford, by burning charcoal in oxygen gas,

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* Philosophical Transactions, 1807.

† Mémoires de l'Institut National, tom. iv. p. 284.

and allowing the carbonic acid gas produced to remain until it had attained the temperature of the oxygen previous to the combustion, found the bulk diminished in the proportion of about $\frac{1}{7}$th of the volume of the oxygen gas consumed. Lavoisier, by a similar experiment with charcoal, thoroughly calcined, found that the oxygen gas suffered a condensation equal only to $\frac{1}{25}$th of its volume. In the experiment of Crawford there appears to be a source of error, from his having operated over lime-water, with which the gas was allowed to remain in contact: in it, as well as in Lavoisier's, some fallacy might be introduced, as Berthollet has suggested, from the absorption of gas by the residual charcoal after the experiment; and in both, the diminution of volume might arise, as he supposes, not merely from the combination of the oxygen with the carbon, but in part from its being combined with the hydrogen he assumes to exist in charcoal, forming water, which would be condensed by its intimate union with the carbonic acid. Guyton, in the combustion of the diamond, obtained a result nearly the same as Crawford's, the diminution of volume amounting to $\frac{1}{7}$th of the volume of the oxygen gas. Messrs Allen and Pepys found, however, in their experiments, that there was no perceptible condensation whatever; that in operating on oxygen gas transmitted repeatedly over ignited charcoal so as to be converted into carbonic acid gas, the volume of gas at the end of the experiment was exactly the same as at the commencement; and as their apparatus appears to have been extremely perfect, this result may perhaps be depended on.

As the attraction of carbon to oxygen appears superior to that of oxygen to any other body, charcoal abstracting oxygen from every other combustible, it seemed not possible to effect the decomposition of carbonic acid. Mr Tennant, however, succeeded in effecting this, by the united force of two attractions, and thus demonstrated its composition by analysis.

Mr Tennant observed, that it has been long known that when phosphoric acid is combined with lime it cannot be decomposed by heating it with charcoal; for though the oxygen of the acid is more strongly attracted by the carbon than by the phosphorus with which it is combined, yet, as it exists in the phosphate of lime, it is retained by two attractions, by that for phosphorus, and by that which the phosphoric acid has for the lime, and it cannot be separated unless both these attractions are overcome. As these joint attractions, then, are more powerful than that of carbon for oxygen, it occurred to Mr Tennant, that if they were made to operate on carbonic acid, its decomposition might be effected, especially if their action were promoted by a high temperature. The experiment suggested by this idea was attended with success. Into a glass tube closed at one end, and coated with sand and clay, to prevent the sudden action of the heat, a little phosphorus was introduced, and over this a little marble in powder, (marble being a carbonate of lime); the tube was then nearly, but not entirely, closed. Heat was applied to it, so as that the end of the tube was raised to a red heat, and kept so for some minutes. When the tube was cold, it was broken, and was found to contain a black powder consisting of charcoal mixed with phosphate of lime,—a proof that the carbonic acid had been decomposed *. The charcoal thus obtained was perfectly similar to the charcoal of vegetables. On deflagrating it with nitrate of potassa in a glass retort it afforded carbonic acid.

This experiment was repeated by Dr Pearson, and varied so as to obtain the most satisfactory results. He found, that when the carbonic acid was combined, not with lime, but with potassa or soda, the decomposition of it was more easy and complete, as the attraction between the carbonic acid and either of the alkalis is not so strong as between it and lime. With soda the attraction is weakest, and at the same time a large quantity of carbonic acid is combined with it, so that from a given quantity of carbonate of soda a considerable quantity of charcoal may be obtained. With this, Dr Pearson made his principal experiment.

Into a coated glass tube, closed at one end, were introduced 200 grains of transparent phosphorus; and 800 grains of carbonate of soda, from which the water had been previously expelled by a very moderate heat, were pressed down upon the phosphorus. The part of the tube containing the alkali was heated red hot over a small portable furnace to within two or three inches of the phosphorus. This part, also, together with that in which the phosphorus was, was gradually drawn over the fire, and kept red hot for twenty minutes. The tube when cold was broken; a solid mass was found in the lower part of it as black as charcoal, weighing 428 grains, and above this a greyish matter, weighing 358 grains. The black matter on being thrown into boiling hot concentrated acetous acid, afforded above 25 ounce measures of carbonic

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* Philosophical Transactions, vol. lxxxi. p. 182.

acid, the soda and phosphate of soda it contained were dissolved, and a quantity of pure charcoal remained, amounting when dried to 32 grains. It had no taste or smell, was extremely light, and by deflagration with nitrate of potassa afforded carbonic acid.

Dr Pearson, by bending the tube at the open extremity, and introducing it under mercury, found, that during the experiment a little nitrogen gas mixed with atmospheric air was disengaged *.

A similar result may even be obtained in the humid way ; if a piece of phosphorus be boiled in a solution of carbonate of soda, perfectly colourless, it becomes black and turbid, from the production of charcoal.

There can be no doubt of the decomposition of the carbonic acid in these experiments. The theory probably is, that the elasticity of carbonic acid in its uncombined state is an obstacle to any affinity exerted to its principles, and hence phosphorus is incapable of attracting its oxygen; if condensed in a combination in sufficient quantity, it is of course more liable to be acted on; and though the affinity exerted to it by the substance with which it is combined tends to preserve its composition, yet if not sufficiently powerful it may be unable to do so : hence the reason why when the acid is combined with soda it is more easily decomposed by phosphorus than when combined with lime. The decomposition, too, may be promoted by the affinity which the base with which the carbonic acid was united exerts to the phosphorus and the oxygen, and in consequence of which they enter into combination with it.

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* Philosophical Transactions for 1792, p. 289.

Carbonic Acid, Mr Davy has found, is rapidly decomposed by potassium from the strong attraction it has to oxygen. It burns in the gas, and precipitates charcoal, and also produces charcoal when heated in contact with carbonate of lime. A partial decomposition of this acid, and its conversion into carbonic oxide, is likewise effected by those metals which have a strong attraction to oxygen, as iron or zinc, the metal being exposed to heat with an earthy carbonate.

Carbonic acid gas is distinguished from the greater number of the gases by its superior specific gravity, which, according to Bergman's experiments, is 0.0018 *, atmospheric air being 0.0012; carbonic acid gas is therefore one-half heavier. 100 cubic inches weigh 46.7 grains, or, according to the more recent estimate by Allen and Pepys, 47.26 grains; it is inodorous; its taste is acid, with a degree of pungency †. It is incapable of supporting combustion, and proves very speedily fatal to animal life. Even when diluted with more than twice its volume of atmospheric air, it can be breathed only for a very short time, as it produces giddiness and faintness. It is formed in the respiration of animals, and is contained in considerable quantity in the air they expire, as Dr Black in his investigation of its properties discovered by experiment.

Carbonic acid gas is absorbed by water; the water under a medium atmospheric pressure, and at a temperature of 50°, absorbing a quantity scarcely equal to, and at 41°

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* Essays, vol. i. p. 83.

† Davy's Researches, p. 472.

rather more than, its own bulk; or, as Mr Henry (from attending to the residual gas after the absorption) has stated it somewhat differently, 100 cubic inches absorbing at 60° 108 of gas.

The union is promoted by agitation and cold. Exposed to the atmosphere, the greater part of the gas slowly escapes, and at a temperature of 212° the greater part or the whole of it is immediately expelled. Freezing also separates it completely. By increasing the pressure, the quantity absorbed is much increased, conformable to the law observed in the absorption of all aërial fluids. The water can thus be made to absorb three times its volume. The water, when combined with an equal volume of the gas, acquires an acidulous somewhat pungent taste, and sparkles much when shaken. Its specific gravity is to that of distilled water as 1.0015 to 1000 *.

The acid powers of this gas, judging from its obvious properties, do not appear to be considerable. Its taste, either in its gaseous form, or combined with water, is slightly acidulous; it reddens none of the vegetable colours except the most delicate, the infusion of litmus †; and it acts with no energy on inflammables or metals. Berthollet, however, ascribes to it a very high acid power, superior even to that of sulphuric acid, in conformity to

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* Bergman's Essays, vol. i. p. 11.

† The infusion of litmus is reddened by a quantity of carbonic acid gas, not exceeding 1-50th of its volume, and one part of water saturated with the acid tinges red 50 parts of the dilute infusion. The tint is fugitive, as the carbonic acid escapes when the liquor is exposed to the air.

the principle on which he supposes the powers of acids are most unequivocally determined, that of saturating the opposing properties of alkalis or earths, a smaller quantity of this acid being requisite to saturate lime or barytes than of sulphuric acid. The weakness of its action, in conformity to this view, must be ascribed to its elasticity, and its strong tendency to pass to the elastic state even when combined with water; and hence, in its combinations with the alkalis, there is always a tendency to an excess of base, so that the alkaline properties are not saturated; and hence also the apparent weakness of its affinities. It may be doubted, however, whether this explanation is perfectly just; for even in the alkaline combinations, when care is taken to have them saturated with the acid, the alkaline properties are only weakened, scarcely fully neutralized.

Carbonic acid combines with the alkalis, forming salts, which, in conformity to the principles of the modern chemical language, are named Carbonates. As the acid powers which carbonic acid actually exerts, are, from whatever cause, weak, the changes which it occasions in the properties of the alkalis are in general inconsiderable. They retain, for example, their peculiar taste and acrimony, at least to a certain extent; ammonia has still its penetrating odour, and in part its volatility; they still, even when saturated with it, change the vegetable colours to a green; they combine with oils, forming imperfect soaps, and the presence of the carbonic acid scarcely opposes any obstacle to the combinations of their bases with the other acids. The changes produced in the earths are more considerable, but still in some of them several of the original properties appear to be retained.

From this circumstance,—the inconsiderable change produced in the alkalis, by their combination with carbonic acid, and from the existence of this acid being unknown, the older chemists formed erroneous notions respecting the nature of these combinations, which gave rise to an inconvenient nomenclature, not yet altogether exploded. The alkalis, when combined with carbonic acid, they termed Mild Alkalis, when in their pure state Caustic; these two they considered merely as modifications of the alkali. They even regarded it as in its purest state when combined with carbonic acid; the causticity belonging to it being ascribed to some change produced in it by the heat, by which it was rendered caustic, or the carbonic acid expelled. Dr Black first pointed out the error of these opinions, and communicated precise ideas on the subject. He discovered that the mild state, as it was termed, of the alkalis and earths, was owing to their combination with carbonic acid, or as he named it fixed air; that, therefore, when they existed in that state, they are real compounds, and that, on the contrary, when in the caustic state, they are pure and uncombined. Bewly and Bergman afterwards demonstrated that this fixed air is an acid, and that therefore the compounds of it with the alkalis and earths, or, according to the old language, the mild alkalis and earths, are neutral salts.

The distinguishing character of this order of neutral salts, is their property of effervescing, on the addition of any acid. This is owing to the attraction of the carbonic acid to the alkali or earth being so weak, or its tendency to elasticity being so great, that it can be displaced even by the weakest acid, and in the moment of its separation it assumes the gaseous form, rises through the liquor, and occasions what is termed Effervescence. The alkaline carbonates, as has been stated, retain the property of changing the vegetable colours to a green, and indeed to a certain extent nearly all the properties of their bases in their pure state. The carbonates of potassa and soda are decomposed by a high temperature, as are also the earthy carbonates, the carbonic acid assuming the elastic form. The decomposition of the earthy carbonates requires a very high temperature, and neither in them nor in the alkaline carbonates is it complete; the increase in the relative quantity of the base, as the decomposition proceeds, adding so much to the strength of the affinity, as to put a stop to it before all the acid is expelled. It is facilitated by the admixture of charcoal, which converts the carbonic acid into carbonic oxide, and hence the explanation of a fact observed by Dr Black, with regard to carbonate of lime, and by Dr Hope, with regard to carbonate of barytes, that the decomposition by heat does not succeed in an earthen, but in a plumbago crucible.

As carbonic acid is diffused through the atmosphere, the alkalis and the earths, which have an attraction for it, can never be found pure in nature, since, if free from every other substance, they would soon be saturated with it. Several earthy fossils are accordingly combinations of this acid.

SUB-CARBONATE OF POTASSA.—Potassa, in the processes by which it is usually prepared, and of which an account has been already given, is always combined with carbonic acid. Thus, in the incineration of vegetables, the usual process, as carbonic acid is formed during the imperfect combustion, it is attracted by the potassa, and this compound forms the principal part of the potash or pearl-ash of commerce.

It is not, however, saturated with carbonic acid, and is therefore not the real neutral salt or carbonate, but a sub-carbonate. But, as it is more generally used in the processes of chemistry than the carbonate, it will not be improper to describe its properties, before proceeding to the consideration of the other.

The potash of commerce, it has already been remarked (page 193), is a heterogeneous substance, consisting, besides the sub-carbonate of potassa, which may be regarded as its basis, of muriate and sulphate of potassa, and of some earthy and metallic matter, the proportions of which are various in different specimens. It is hence an object of considerable importance, in practical chemistry, to be able to determine, by an easy and accurate method, the quantity of alkali in an active state, in a given weight of potash or pearl-ash. A process of this kind was given by Mr Kirwan, in his treatise on the art of bleaching. It consisted in adding a solution of alum in 3 or 4 parts of warm water, while hot, to a solution, likewise warm, of an ounce of the potash or pearl-ash submitted to trial, dissolved in 1 lb. of water; the addition being continued until the liquor indicates a sensible acidity by its effect, on a delicate vegetable colour; the whole is poured on a filter of bibulous paper, and the precipitate which has been formed is washed with water, until the water pass through tasteless; the earth remaining on the filtre is dried, first by a gentle heat, and afterwards by exposure to a temperature of 400 or 500. The weight of this, it might be presumed, would afford an indication of the quantity of alkali to which its precipitation was owing; but it is necessary to expel from it the carbonic acid combined with the argil, which might be variable from different specimens of potassa. This Mr Kirwan does, by adding to it muriatic acid. The dried precipitate is put into a Florence flask, and weighed; about an ounce of muriatic acid, (where an ounce of pearl-ash has been originally submitted to trial), is put into another flask, and both flasks are put into the same scale of a balance, counterpoising them by weights in the opposite scale; the acid is then poured gradually into the flask containing the precipitate; and, after the effervescence is over, and the vessel has stood a short time, the weight is to be taken which is necessary to add to the scale on which the flasks are placed, to restore the equilibrium; this weight is to be subtracted from that of the earth, and the remainder is a weight exactly proportioned to the weight of alkali, in the specimen of potash or pearl-ash submitted to trial. The comparative quality of different specimens can thus be ascertained *.

Vauquelin has given another method, which has the advantage of ascertaining not only the quantity of alkali, pure,

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* The same method may be applied to determine the quantity of alkali, pure or combined with carbonic acid, contained in different specimens of barilla or kelp. It cannot, however, be regarded as accurate, as part of the earths in the potash or barilla may be precipitated when the alkali is saturated, and as argil retains very different quantities of water in drying.

or combined with carbonic acid; but, by some additional steps, the quantity combined with sulphuric and with muriatic acids, these compounds being of equal utility as the pure potassa, in some of the purposes to which it is applied, as in the preparation of alum or of nitre, and perhaps also in the manufacture of glass. The first step, that of ascertaining the quantity of potassa, pure, or combined with carbonic acid in the potash, is founded on the quantity of an acid, nitric acid for example, that a given weight of the alkali may be able to saturate. This is the simplest mode, but the difficulty is to fix on a standard acid, always uniform. The method Vauquelin employs, is to take a quantity of potassa, purified by the process of Berthollet, and perfectly dry, to saturate it exactly with nitric acid, the specific gravity of which is ascertained; then to take this acid as a standard for proving the different kinds of potassa which may be submitted to trial, a given weight of any of these being dissolved in water, and a portion of the acid being added with care, so as to attain exact neutralization, heating the liquor at the same time gently, to expel any carbonic acid that might be retained. To know the quantity of alkali contained in the specimen examined, nothing more is requisite than to compare the quantity of acid consumed in the operation, with that which was necessary for the neutralization of the pure potassa. To discover, farther, the quantity of alkali combined with sulphuric acid, Vauquelin employs a solution of nitrate of barytes, which he adds to the solution neutralized by the nitric acid, as long as any precipitate is formed; the weight of the sulphate of barytes, when collected and dried, giving the quantity of sulphuric acid, and of course of sulphate of potassa, according to the known proportions of these salts; the quantity of sulphate of barytes corresponding to one-half its weight of sulphate of potassa, and to $\frac{23}{100}$dths of the potassa contained in the latter. And, lastly, to discover the quantity of potassa combined with muriatic acid, he adds to the solution which has undergone the preceding operations, a solution of nitrate of silver, the weight of the precipitate of the muriate of silver, dried, giving the quantity of muriatic acid, and of course of muriate of potassa, according to the established proportions of these compounds. Vauquelin has added the following table of the analysis of different kinds of potash met with in commerce, by these methods *.

	Potassa.	Sulphate of potassa.	Muriate of potassa.	Insoluble residue.	Carbonic acid and water.	
Russian potash,	772	65	5	56	254	=1152
American ditto,	857	154	20	2	119	=1152
Pearl-ash,	754	80	4	6	308	=1152
Treves potash,	720	165	44	24	199	=1152
Dantzic potash,	603	152	14	79	304	=1152
French potash,	444	148	510	34	304	=1152

This method, however, is probably still too complicated to be employed by the common manufacturer. One more simple, for determining the quantity of potassa, pure, combined with carbonic acid, or with sulphuric acid, (in all which states it is of equal advantage in the preparation of

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* Annales de Chimie, tom. xl. p. 284.

nitre from the materials of nitre beds, as the alkali in either combination is still capable of decomposing the nitrate of lime), has been given by the administrators of the saltpetre works in France : It consists in adding a solution of nitrate of barytes or strontites, which is decomposed either by the pure alkali, or by the carbonate or sulphate *. This may answer for this purpose ; but there is still wanting, what is chiefly of importance in the different arts in which potash is employed, an easy method of determining the proportion of potassa pure, or combined only with carbonic acid.

To remove the sulphate and muriate of potassa in the potash of commerce, and obtain the sub-carbonate, it is dissolved in an equal weight of warm water, the clear solution is poured off from the undissolved matter, and is evaporated in a clean iron or silver bason until a pellicle appear on its surface ; it is removed and allowed to stand for some hours, when a little muriate of potassa is deposited ; the clear liquor is poured off, and is then evaporated to a dry mass, which is reduced to a coarse powder. Another process for preparing it, formerly, and still sometimes employed, is that of burning the salt, known by the name of Tartar, which is deposited from wines in the cask, and which consists of potassa united with a vegetable acid, the Tartaric. This acid having carbon and hydrogen for its base, a portion of carbonic acid is formed in the decomposition it suffers at a high temperature, which remains combined with the alkali, forming a sub-carbonate. This is separated from the carbonaceous matter by solution in water, and, by evaporation, obtained in a concrete state. From being prepared in this way, it was formerly named Salt of Tartar. It was also obtained sometimes by deflagrating the tartar with nitrate of potassa; or by deflagrating this latter salt with charcoal, the nitric acid being decomposed in the deflagration, and carbonic acid formed which is attracted by the potassa. As obtained by these processes, the sub-carbonate is purer than as obtained from the pearl-ash of commerce, the latter always containing sulphate of potassa and siliceous earth. That obtained by a low red heat from tartar was supposed, by Dr Black, to be the most mild, or to contain the largest quantity of carbonic acid.

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* Annales de Chimie, tom. xli. p. 113.

The sub-carbonate of potassa purified by solution in water, and obtained in a concrete state by evaporation, is generally in the form of coarse grains, of a white colour; as it is not easily susceptible of crystallization. From the excess of alkali it contains, it is deliquescent; if exposed to the air, it soon becomes humid; and if exposed for a sufficient length of time, attracts as much water as dissolves it. Its taste is acrid; it changes the vegetable colours to a green, and combines with oils, forming a saponaceous compound. It is decomposed by the acids; its carbonic acid being disengaged with effervescence. A considerable portion, but not the whole of its acid is expelled by a strong red heat.

According to Mr Kirwan, common sub-carbonate of potassa contains about 60 of alkali, 28 or 30 of carbonic acid, and 6 of water, with a few grains of siliceous earth, sulphate of potassa, and argil.

Carbonate of Potassa.—This was obtained by the older chemists, though they were unacquainted with its nature, by exposing sub-carbonate of potassa to the air until it passed into solution, and leaving the solution exposed for a number of months; carbonic acid was slowly attracted from the atmosphere, and crystals of the neutral carbonate were deposited. It can be obtained more quickly by exposing a strong solution of the sub-carbonate to an atmosphere of carbonic acid, such as that collected over the surface of fermenting liquors, or passing through it a current of this gas, disengaged from marble, and diluted sulphuric acid, interposing a bottle with water, to detain any minute quantity of sulphuric acid that might be elevated by the violence of the effervescence. In either case the solution ought to be of such a strength (one part of sub-carbonate to three of water) that when saturated, it crystallizes spontaneously, as the crystallization cannot be promoted by evaporation, a heat not greater than that of boiling water partially decomposing the salt, and disengaging a little carbonic acid. As the saturation of the alkali with the acid proceeds, a light earthy precipitate is formed, consisting, as Pelletier has shewn, of silex that had been combined with the alkali, and which is most effectually separated by this process. Another process to prepare this salt was given by Bergman;—mixing a solution of the common sub-carbonate of potassa with a solution of carbonate of ammonia in a retort, and applying heat; the ammonia is expelled, and the potassa saturated with carbonic acid crystallizes as the liquor cools. To Bergman and Pelletier we are principally indebted for its history.

The crystals of carbonate of potassa are bevelled quadrangular prisms; they do not, like the sub-carbonate, deliquesce; and, according to Bergman, they are not efflorescent. They require, at a mean temperature, four parts of water for their solution, and produce, while dissolving, a degree of cold. They are much more soluble in hot water, the water taking up even $\frac{5}{6}$ of its weight; but if the temperature be that of boiling water, part of the carbonic acid assumes the elastic state, and rises through the liquor. Exposed to a moderate heat in a dry state, the crystallized salt splits, then fuses, parts with its water of crystallization, and yields part of its carbonic acid.

The taste of the neutral carbonate of potassa is more mild than that of the sub-carbonate, though still alkaline; it has no causticity, but it unites with oils, and changes the vegetable colours to a green.

According to Bergman, it consists of 48 of potassa, 26 of carbonic acid, and 32 of water *. The proportion of acid is in this estimate probably stated too low. Bergman estimated it from the loss of weight the crystals sustained by a slow solution in acids, a method liable to fallacy from part of the carbonic acid being retained in the liquor. Pelletier gives as the proportions, 40 of potassa, 43 of carbonic acid, and 17 of water †.

It is decomposed in the humid way by lime, barytes and strontites, which instantly attract the carbonic acid, forming insoluble precipitates. In the dry way, and with the assistance of heat, silex likewise decomposes it, combining with the alkali, and forming a glass variable in its qualities according to the proportions, the carbonic acid

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* Essays, vol. i. p. 18.

† Mémoires, t. ii. p. 430.

being expelled. It is also immediately decomposed by the acids, which disengage the carbonic acid gas from the alkali with a rapid effervescence.

The carbonate of potassa is scarcely used but for some medicinal purposes, but the sub-carbonate, especially in the state of the potash and pearl-ash of commerce, is applied to many uses, principally from the alkali it contains. It is thus used in the process of bleaching to extract the colouring matter of the thread, and in dyeing to heighten some of the colours. It is employed in the manufacture of soap, and, with siliceous earth, forms the finer kinds of glass.

Potassa appears capable of combining with a portion of carbonic acid, inferior to that which neutralizes it, but still so as to form a crystallizable salt. It is remarked by Steinacher, that if the saturating of the solution of the sub-carbonate with carbonic acid be stopt, when the siliceous earth appears to be deposited, the liquor evaporated by a gentle heat affords crystals in plates, which so far differ from the neutral salt as to deliquesce.

The alkali can be easily super-saturated with carbonic acid. This is done by dissolving the sub-carbonate in water, (one ounce in ten pounds), and by the assistance of cold and pressure impregnating the solution strongly with carbonic acid gas. This has been used in medicine under the name of Aërated Potash Water; its taste, when a sufficient quantity of carbonic acid has been combined in it, is pleasantly acidulous, with some pungency, and the alkali thus super-saturated proves less irritating to the stomach than in any other state. Different kinds of apparatus have been employed to prepare it, particularly that invented by Dr Nooth, described in the 65th volume of the Philosophical Transactions. It may also be prepared in a range of Woulfe's bottles, in which, by a sufficient immersion of the tubes in the liquid, the necessary pressure is obtained. Other kinds of apparatus, in which still greater pressure can be obtained, so as to bring a larger quantity of carbonic acid into combination, are employed by some chemical artists, which, however, have not been made public.

Carbonate of Soda.—The sub-carbonate of Soda has not been observed; the alkali, in its production from the incineration of marine plants, being saturated with carbonic acid, or at least a neutral carbonate of soda crystallizing with facility from the ley of the Barilla. This is the process which is generally employed for its preparation,—the purer kinds of barilla being lixiviated with water, the clear solution poured off and evaporated. By cooling, it affords crystals of carbonate of soda.

This salt, it has already been stated, is found native in India, Egypt, and Syria, in the form of crystalline masses, or of an efflorescence, and, in the lakes of Egypt at least, obviously derives its origin from the decomposition of muriate of soda, exposed under favourable circumstances to the action of carbonate of lime.

Carbonate of soda crystallizes in octohedrons, composed of two four-sided pyramids joined by the base, which are truncated at the summits of the pyramids; and also in rhomboidal plates. Its taste is alkaline, but not acrid, and it changes to a green the vegetable colours. It is efflorescent, so as in a dry atmosphere to be soon reduced to a powder. It requires, at a medium temperature, twice its weight of water for its solution, and is more abundantly soluble in hot water, its saturated solution crystallizing on cooling. Exposed to heat, it suffers the watery fusion from the large quantity of water of crystallization which it contains; as this is dissipated, it appears as a dry white powder, which by an increase of heat may be fused and partially decomposed.

The proportions of the constituent principles of this salt, are stated by Kirwan at 21.58 of soda, 14.42 acid, and 64 water of crystallization, with which the estimate of Bergman almost precisely agrees.

This salt suffers decompositions similar to the carbonate of potassa, from other chemical agents, as from lime, barytes, and strontites, and from the acids. It is applied nearly to the same uses. It is even preferred in the manufacture of glass, and in soap-making it affords a soap which becomes concrete, while that from potassa remains soft. In these arts, it is used under the form of barilla, and what in this country is named kelp, which is merely an impure barilla obtained by burning the different varieties of sea-weed. A purer carbonate of soda has also, within these few years, been introduced into the market, obtained by various processes to be afterwards described, from the decomposition of sea-salt, of which soda is the base.

Soda is super-saturated in solution in water with carbonic acid, and under this form is medicinally employed as an antacid and lithontriptic. It is even more used than potassa, on the supposition that it is more mild and pure. As the crystallized carbonate of soda contains less real alkali than the sub-carbonate of potassa, double the quantity of it is added to a given quantity of water previous to the super-saturation with carbonic acid. The common proportion is two ounces to ten pounds.

Carbonate of Ammonia.—Ammonia, by saturation with carbonic acid, has its properties nearly, but not altogether, neutralized. A salt is formed, which though volatile, exists in a concrete state: It retains the pungent ammoniacal odour and taste, is slightly caustic, and changes the vegetable colours to a green.

This salt may of course be formed by the direct combination of its principles. On mixing ammonia and carbonic acid, each in its gaseous state, they instantly combine, and form the concrete salt. It is more usually obtained, however, economically, in an indirect mode, by decomposing muriate of ammonia, a salt prepared on a large scale for various uses to which it is applied.

Equal parts of chalk, which is merely a carbonate of lime, dried, and of muriate of ammonia, are mixed together, and put into an earthen retort, or an iron pot, to which a capital is adapted, and which is connected with a large receiver. Heat is applied, by which a double decomposition is effected. The lime, on the one hand, attracts the muriatic acid, and the ammonia, on the other, the carbonic acid. The muriate of lime which is formed remains in the vessel, and the carbonate of ammonia being volatilized, is condensed on the sides of the receiver in the form of a crust. In this manner, the solid carbonate of ammonia is prepared on a large scale in pharmacy.

There is another process likewise frequently performed, in which it is obtained in solution in water. Equal parts of muriate of ammonia and of sub-carbonate of potassa are put into a retort with 2 parts of water, and heat applied; a double decomposition likewise takes place in this case, the muriatic acid uniting with the potassa, and the carbonic acid with the ammonia; the carbonate of ammonia passes over along with the aqueous vapour, which, when condensed, is sufficient to dissolve it.

Carbonate of ammonia is also obtained in large quantity in the decomposition of animal matter by heat. If bones be put into an iron still, the decomposition of the gelatin they contain affords both ammonia and carbonic acid, and hence a large quantity of carbonate of ammonia is procured. This is the salt of hartshorn of the older chemists. It is impure and fœtid from a portion of empyreumatic oil, likewise formed in the decomposition of the animal matter; from this it is partially freed by sublimation from chalk, and completely by sublimation from charcoal.

Carbonate of ammonia is very soluble in water; at a mean temperature it requires only twice its weight, and at 212° less than its own weight is sufficient for its solution. Its saturated solution, on standing for some time, deposites crystals, the figure of which is not easily discovered, but appears to be octohedral. Exposed to a very moderate heat, it is entirely volatilized; it is however easily condensed, and its deposition on the sides of the vessel is of a regular dendritical form. It effloresces on exposure to the air, and its odour becomes weaker, perhaps, from the loss of its moisture, or from the absorption of a still greater quantity of carbonic acid.

According to Bergman, it consists of 43 of alkali, 45 of acid, and 12 of water. Kirwan in one experiment found it to be composed of 24 ammonia, 52 carbonic acid, and 24 of water *; but, as he remarks, it is known to exist in very different states. Mr Davy observed that the proportions vary in different specimens, from 20 to 50 parts of alkali in 100. The carbonic acid and water are superabundant in it, as the temperature at which it has been formed is low, and the alkali, as it has been high; that formed at 300 contained above 50 of alkali in 100 parts, while that produced at 60 contained only 20 †.

Carbonate of ammonia is decomposed by the two fixed alkalis, barytes, strontites and lime, which all combine with its acid. Magnesia effects a similar decomposition in it, but only partially. The acids attract its base, and expel the carbonic acid with effervescence.

This salt is used in medicine as a stimulant and diaphoretic, and as a stimulating perfume.

Carbonate of Barytes exists native, and is prepared artificially, either by adding carbonic acid to barytic water, or by decomposing muriate of barytes by an alkaline carbonate. It exists as a white powder, of considerable specific gravity; it is not soluble in water in any appreciable quantity, but is dissolved in small quantity when the water is impregnated with carbonic acid. This salt is somewhat differently affected by heat, according as it is in its native state, or has been artificially prepared. The latter is more easily decomposed, or its carbonic acid is more easily and completely expelled, owing, as has been supposed, to the presence of water in the artificial carbo-

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* Transactions of the Irish Academy, vol. vii. p. 267.

† Researches, p. 76.

nate, and to water being necessary, as has also been supposed, to the constitution of the gases. It was even stated by chemists, particularly by Withering and Pelletier, who analyzed the native carbonate, that it does not part with its carbonic acid in the most intense heat. Dr Hope, however, shewed that this is an error. It is difficult, indeed, to decompose it by heat in a clay crucible, as the barytes, and the earth of the crucible, act as mutual fluxes; but, exposed in a black-lead crucible to the heat of a forge, Dr Hope found that the carbonic acid could be expelled from it. It might be supposed, perhaps, that the carbonaceous matter of the plumbago crucible might favour the operation, by causing the decomposition of the acid; but this could scarcely have much effect, and Dr Hope, in one experiment, succeeded in expelling the carbonic acid completely in a crucible of clay. Klaproth could expel it only partially in a platina crucible.

Carbonate of Strontites is formed, on adding carbonic acid, or a solution of an alkaline carbonate, to a solution of strontites, or of a strontitic salt. Being insoluble it is precipitated. With an excess of acid it becomes soluble. The artificial carbonate, like that of barytes, is more easily decomposed than the native.

Carbonate of Lime.—This is an important compound existing in nature in great abundance and under a variety of forms. It is formed, by adding carbonic acid to lime-water; by agitating water impregnated with that acid with lime, or by decomposing any of the soluble salts of lime, by any of the alkaline carbonates. But its chemical properties are generally described from those varieties of it which exist native in a state of purity, particularly from calcareous spars, or from some of the varieties of marble, in which no ingredient can be discovered but carbonate of lime.

It is perfectly insipid: it appears also, in its neutral state, to be insoluble in water, or at least very sparingly soluble; but, by an excess of carbonic acid, it may be dissolved: thus, if liquid carbonic acid be added to lime-water, a milky precipitate is at first formed; but if more of the acid be added, this is redissolved, and the liquid becomes limpid. On leaving it exposed to the air, however, the excess of carbonic acid escapes, and the neutral carbonate is again precipitated.

When exposed to heat, carbonate of lime first loses what water it contains, and, if transparent and hard, becomes white, opaque, and friable. If the heat be augmented, the carbonic acid is expelled, and pure lime remains. This operation is performed on a large scale, on the different varieties of the native carbonate, marble, chalk, and more particularly limestone, to obtain lime for the numerous uses to which it is applied. The heat is applied to the limestone in a kind of open furnace or kiln, and some care is requisite that it should not be applied in too high a degree, as vitrification of the lime, by which it would be rendered incapable of slaking, might happen, from the influence of the argillaceous or siliceous earth which limestone contains. The same caution is requisite, when the experiment is performed on a small scale in a crucible; and indeed to obtain pure lime from the carbonate, it is necessary that the decomposition by heat should be done in an iron-pot, or in a platina-crucible.

The experiments of Sir James Hall have proved, that if the separation of the carbonic acid from its combination with the lime be prevented by the requisite pressure, carbonate of lime may be fused, and by a heat comparatively moderate, intermediate between 20° and 30° of Wedgwood's scale, according to the more or less perfect compression. The result is a substance possessing considerable hardness and closeness of texture, and approaching by these qualities, as well as in fracture and specific gravity, to the finer kinds of limestone or marble *. Bucholz has since discovered, that even without compression carbonate of lime under particular circumstances is fused. He had exposed a large quantity, 4½ lbs., of pure washed chalk, in a Hessian crucible, to a red heat, not gradually raised, for an hour in a wind furnace. A thin layer on the surface, and next the sides of the crucible, was converted into lime; but this was followed almost to the centre by laminæ adhering strongly, very hard and solid, half fused, and of a yellowish white colour; under this was another part extending to the bottom of the crucible, having still more decided marks of fusion; its fracture when it was broken being smooth and conchoidal, and its hardness such as to cut glass; some fragments were even transparent. This fused chalk Bucholz found had not lost more than one *per cent.* of its acid †.

Carbonate of lime is decomposed by the acids with sudden effervescence, from the expulsion of the carbonic acid in the elastic state. This property of effervescing on the contact of an acid, though it may be discovered by the application of a very concentrated acid to some other salts, particularly the fluates and muriates when in powder, is much more conspicuous in the carbonates, and affords a discriminating character of carbonate of lime.

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* Edinburgh Philosophical Transactions, vol. vi.

† Nicholson's Journal, vol. xvii. p. 230.

Pure native carbonate of lime consists, according to Mr Kirwan, of 55 of lime, and 45 of acid; which he supposes to be also the proportion of the artificial carbonate, when exposed to such a heat as to expel its water.

Carbonate of Magnesia.—This is a compound of some importance from its medicinal use. It is the Magnesia Alba of physicians, and was introduced into the practice of medicine about the beginning of the last century. At first it was prepared by evaporating to dryness the liquor remaining after the crystallization of nitre: this contained the nitrate of magnesia, which was decomposed by heat, the nitric acid being expelled. The magnesia thus obtained, however, was always mixed with lime and other substances. The more advantageous method was afterwards discovered, of preparing it by decomposing the magnesian salts, by the alkaline carbonates; and this is the process which is now employed.

In the directions given in the Pharmacopœia for its preparation, equal weights of sulphate of magnesia and subcarbonate of potassa are dissolved separately in twice their weight of water; the solutions are strained, mixed together, and immediately diluted with 8 parts of warm water: the magnesia attracts the carbonic acid; and the compound being insoluble, is precipitated, while the sulphate of potassa that is formed remains in solution. The mixture is made to boil for a few minutes: after cooling a little, it is poured upon a cloth: the clear fluid runs through: the white precipitate of carbonate of magnesia remains, and it is washed with water till it is tasteless.

In this country, the manufacture of magnesia on a large scale is conducted by a process somewhat different from this. Instead of the pure sulphate of magnesia, the bittern, or liquor remaining after the crystallization of sea-salt, as it can be had at a much cheaper rate, is used. Some of the manufacturers precipitate it by carbonate of potash, or rather by the impure potashes of commerce; others, by an impure and imperfectly saturated carbonate of ammonia. The bittern is heated to the boiling point: the alkaline solution is added, and the fire is immediately withdrawn. The mixture is moderately stirred, to promote the decomposition. It is then poured on a piece of canvas, stretched over a cistern; the liquor, holding the muriate and sulphate of potassa, or ammonia, strains through: the carbonate of magnesia remaining on the cloth is washed with water till it is tasteless. When the washing is completed, a frame of wood, divided into small squares, is placed upon the thin paste, so as to divide the magnesia. After it has become firm, the drying of it is completed, by placing it in a stove, or over heated flues.

The success of the process, so as to obtain the magnesia very light, smooth, white, and tasteless, depends on a variety of circumstances;—on the purity of the alkali, the mode of precipitation and washing, and the purity and softness of the water with which it is washed. The management of these circumstances is not always perfectly known, and hence we find a considerable difference in the magnesia prepared by different manufacturers.

Carbonate of magnesia, when properly prepared, is perfectly white, nearly, if not entirely tasteless, possessing little coherence in its texture, and of a specific gravity not more than 2.3. It is very sparingly soluble in water; requiring at least 2000 times its weight, at the temperature of 60°. Fourcroy has remarked, that in this state it is not saturated with carbonic acid, as it still absorbs more, when exposed to its action. When acted on by water impregnated with carbonic acid, it is dissolved: when such a solution is allowed to evaporate spontaneously, the carbonate of magnesia is deposited in small hexagonal prismatic crystals, which are transparent and efflorescent. Similar crystals are obtained, by mixing a solution of sulphate of magnesia with a solution of carbonate of potassa, and allowing the mixture to remain at rest: they are deposited at the end of a few hours. These crystals are efflorescent: they are soluble in 48 parts of water, at 60°; and, by slow evaporation, this solution again affords crystals. These consist of 25 of magnesia, 50 of acid, and 25 of water; while the proportions of the common carbonate are, from 45 to 55 of earth, from 25 to 48 of acid, and from 15 to 30 of water. Carbonate of magnesia is decomposed by heat, its carbonic acid being expelled.

CARBONATE OF ARGIL can scarcely be formed. Water impregnated with carbonic acid dissolves, according to the younger Saussure, a portion of the earth, but in evaporating the solution, the carbonic acid is expelled; and the carbonate cannot therefore be obtained in a solid state. In decomposing an argillaceous salt by an alkaline carbonate, the argil which is precipitated has a portion of carbonic acid combined with it.

The other earthy carbonates are scarcely known. CAR-

BONATE OF ZIRCON is insoluble. CARBONATE OF GLUCINE is obtained by decomposing the solution of a salt of glucine by an alkaline carbonate. It is precipitated in a soft state, and is not easily dried; is insipid, insoluble in water, and is not rendered soluble by an excess of acid. It is decomposed by heat. Solutions of the salts of ITTRIA are decomposed by alkaline carbonates, a white precipitate, which is probably carbonate of ittria, being thrown down.

Carbonic acid, in its gaseous state, does not act on any of the metals, but water impregnated with it dissolves small portions of iron and zinc. By indirect modes it can be combined with the oxides of the other metals, forming compounds afterwards to be described.

SECT. V.

OF CARBONIC OXIDE.

CHARCOAL, in burning, saturates itself with oxygen; and passes to the state of an acid, and hence the existence of any intermediate compound of carbon and oxygen was not suspected. It has been discovered, however, that this acid, by being exposed at a high temperature to the action of substances which have a strong attraction to oxygen, as well as by some other processes, is converted into a gas, inflammable, and having no acid properties. This has been supposed owing to a partial abstraction of oxygen from the carbonic acid, and hence this gas has been regarded as an oxide of carbon, particularly by Cruickshank, and by Guyton, and Clement and Desormes. Other chemists, particularly Berthollet, have supposed, that a portion of hydrogen enters into its composition. Though the determination of this question is attended with difficulty, the former opinion is perhaps the more probable one. The presence of hydrogen has rather been inferred from theoretical views than from experimental proof, and if it be present, it is in a quantity not appreciable. I have, therefore, at least in the present state of our knowledge with regard to it, adopted the views of Mr Cruickshank, and considered it as a gaseous oxide of carbon.

For our knowledge of this compound, we are indebted to experiments suggested by some objections urged by Dr Priestley against the modern theory of chemistry. He had observed, that in exposing to heat mixtures of gray oxide or scales of iron with charcoal, or with the compound of carbonic acid and barytes, large quantities of gas are disengaged, inflammable, and which he regarded as analogous to the heavy inflammable air, or carburetted hydrogen of the new nomenclature; he considered its production, therefore, as a proof of the presence of water in the oxide of iron, a position which he had maintained in his views of chemical theory. His experiments were repeated by Dr Woodhouse of Philadelphia, and the results, so far as related to the production of an inflammable elastic fluid, confirmed *. Dr Woodhouse ascertained, too, that although in the first stage of the process in which mixtures of charcoal with metallic oxides are exposed to heat, the inflammable gas was accompanied with carbonic

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* Annales de Chimie, tom. xxxviii. p. 271.

acid, towards the end it was perfectly free from it. His memoir, transmitted to the French National Institute, had excited the attention of some of its members; a series of experiments on the subject was made by Berthollet *, and others by Clement and Desormes †. But previous to this, Mr Cruickshank had entered on the investigation, had shewn that the elastic fluid disengaged in Dr Priestley's experiments is different from what he had supposed it to be, and had established the principal facts as to its production and analysis ‡.

If, according to the original experiment of Dr Priestley, a mixture of the gray oxide or scales of iron, and of charcoal, (each having been previously exposed in a covered crucible to a red heat, and the mixture of them made while they are hot), be introduced into a coated glass retort, on raising it to a red heat a large quantity of elastic fluid is disengaged, which, as obtained at different stages of the process, is somewhat different. The first portion consists, according to Mr Cruickshank, of one part of carbonic acid, and four parts of inflammable gas; the second and third portions of one part of the former, with five of the latter, and after that to the end only one part of carbonic acid is found in seven of inflammable gas. The quantity in all, he remarks, is prodigious,—amounting to many gallons by measure from two ounces of materials. A similar production of gas takes place, as Woodhouse had ascertained, from mixtures of other metallic oxides,

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* Mémoires de l'Institut National, t. iv.

† Journal de l'Ecole Polytechnique, tom. iv. p. 323.

‡ Nicholson's Journal, 4to, vol. v. p. 3.

those of zinc, copper, lead, manganese or bismuth, with charcoal, treated in the same way. From the mixture with oxide of zinc, the proportion of carbonic acid to the inflammable gas, Cruickshank found to be still less, being at first only 1 to 9, in a second portion as 1 to 26; and afterwards what was received was purely inflammable. From mixtures of oxide of copper and litharge, the results were similar to those from iron. In general the oxides which retain their oxygen most strongly, afford the largest quantity of inflammable gas; and those which part with it readily the greatest proportion of carbonic acid. The latter is produced chiefly towards the commencement of the process, the former more abundantly, and in greater purity towards the end. Clement and Desormes found that the inflammable gas was produced by heat, not only from the mixture of a metallic oxide, as that of zinc, with well calcined charcoal, which, when exposed by itself to a strong heat, gave out no gas, but likewise from the mixture of the oxide with plumbago or carburet of iron.

On the supposition that this is an oxide of carbon, its production must be ascribed to the oxygen of the metallic oxide combining with the inflammable matter of the charcoal, the proportion not being such as to saturate the carbon and form carbonic acid. This is the conclusion drawn both by Cruickshank and Guyton. On the theory of Berthollet, as charcoal is supposed to contain hydrogen, this will enter with the carbon into combination with the oxygen of the metallic oxide, and produce what must in strictness be regarded as a ternary compound. The grounds of these opinions will be immediately considered.

The inflammable gas, freed from the carbonic acid by repeated washing with lime water, appears, as produced from these different mixtures, to be the same. It was found to be very little lighter than atmospheric air, its specific gravity being as 22 to 23; a circumstance, which at once establishes a distinction between it and the carburetted hydrogen gases, which in general are about one-half lighter than atmospheric air. It does not explode when mixed with atmospheric air and kindled, but burns with a blue lambent flame; nor does it consume much oxygen in its combustion, 100 cubic inches of it weighing 30 grains, requiring for saturation only 44 cubic inches, or 15 grains of oxygen gas. The products, according to Mr Cruickshank's estimate, are about 76 cubic inches, or 35.5 grains of carbonic acid, and 8 of water; and its composition from this analysis proceeding on the suppositions that water is composed of 15 hydrogen, 85 oxygen, and that carbonic acid contains $\frac{1}{5}$th nearly of pure carbon, he states at 15 oxygen, 7 carbon, and 1 hydrogen. This hydrogen is no doubt derived from the charcoal, but there is no proof whether it exists in immediate combination with the carbon and oxygen of the gas, or only in the state of a carburetted hydrogen mixed with the carbonic oxide. As a carbonic oxide can be obtained by a process to be described, without any appreciable quantity of hydrogen, and as it does not appear to differ in any of its properties from the one obtained from the mixture of charcoal and metallic oxides, the latter conclusion appears to be the more probable one, and must be received by those who admit the existence of a pure carbonic oxide.

The analysis of this gas, obtained from the mixture of oxide of zinc, and well calcined charcoal, performed in the same mode by Clement and Desormes, affords results somewhat different from those of Cruickshank. 100 measures of it required, in their experiment, 35 measures of oxygen gas, and produced 81 measures of carbonic acid gas; whence, on the assumption of Lavoisier as to the composition of carbonic acid, verified by their own experiments, that it consists of 71.65 oxygen, and 28.35 carbon, they conclude that the carbonic oxide is composed of 58.4 oxygen, and 41.6 carbon by weight. This is the mean of a number of experiments, which differed considerably, owing to the quantity of charcoal employed and the temperature; circumstances which gave rise to considerable differences in the proportions of the gas. These chemists produced the same gas, by exposing carbonic acid to a high temperature, in contact with charcoal; as, by heating a mixture of charcoal and carbonate of barytes, or by passing carbonic acid, dried previously by exposure to muriate of lime, over charcoal ignited in a porcelain or glass tube. The gas in the latter experiment requires to be passed repeatedly over the charcoal, to be converted into carbonic oxide; and Deyeux has since proposed an apparatus for this purpose, consisting of several iron tubes, placed horizontally across a furnace, and connected at their extremities *. Chaussier has found that much of this gas is disengaged in the detonation of three parts of nitre and one of charcoal, and in the detonation of charcoal with oxymuriate of potassa; and Hassenfratz discovered that it could be formed directly by pass-

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* Nicholson's Journal, 8vo, vol. xi. p. 116.

ing oxygen gas slowly over calcined charcoal in a tube, in a state of ignition.

Dr Priestley had observed, that an inflammable gas is obtained by exposing to heat a mixture of carbonate of barytes, and gray oxide of iron. The experiment was repeated by Mr Cruickshank; both substances having been previously made red hot for some time, with the same result. When, in place of oxide of iron, he employed dry iron-filings, and mixed them with carbonate of lime (chalk), which had been exposed to a low red heat, the mixture, on being urged with heat, afforded much more gas than the other, which at a medium consisted of 4 or 5 parts of inflammable gas, with 1 of carbonic acid. A mixture of tin filings and carbonate of lime gave a similar result. From clean zinc filings, with carbonate of lime, a very large quantity of gas was given out at a red heat, at first containing a little carbonic acid, but towards the middle and end of the process consisting of inflammable gas perfectly pure.

This gas, from the manner of its production, may be expected to be a purer oxide of carbon than the preceding, as there is no source whence hydrogen, in any sensible quantity, could be obtained. The carbonate of lime or barytes might perhaps be supposed to contain a small portion of water that might afford it; but it is not ascertained that they do contain water, at least in quantity sufficient to form the large quantity of inflammable gas disengaged in these experiments, if hydrogen be essential to its formation, nor if they do contain it in that quantity, is it proved that it would be decomposed; on the contrary, we might expect it to be retained by the lime or barytes, in consequence of the strong affinity they exert towards it; neither, were it disengaged, is it proved, that at the temperature at which the production of carbonic oxide is effected, instead of entering into combination with the gas, it will be decomposed, and its hydrogen combined with the carbon and oxygen of the oxide. It was accordingly found by Mr Cruickshank, as I shall have immediately to state, that no sensible quantity of water is produced in its combustion.

Mr Cruickshank succeeded in obtaining this substance, by a process which appears not less equivocal, and in which we can scarcely suppose it to have received any hydrogen; and it is this fact principally, which I would consider as proving it to be merely an oxide of carbon. The process consists in decomposing carbonic acid, when it is in its full elastic state. This was done in two modes: in one experiment, by placing at the bottom of an iron retort, a quantity of dry and very pure sand; over this a stratum of chalk or carbonate of lime, which had been very carefully dried; above this another stratum of sand, on the surface of which was placed a quantity of very clean iron-filings. On raising the body of the retort to a red heat, gas was disengaged, which at first was chiefly carbonic acid; the second portion, amounting to a gallon, consisted of carbonic acid gas, one part, and gaseous oxide, three parts; the third, which was upwards of two gallons, of carbonic acid two parts, and gaseous oxide seven; and the last contained a somewhat greater proportion of carbonic acid. In a second experiment, the decomposition of carbonic acid, or its conversion into carbonic oxide, was effected by causing it to pass repeatedly through an iron-tube, filled with iron-wire, raised to a red heat; by continuing this sufficiently long, not less than three-fourths of the carbonic acid were converted into carbonic oxide. In both experiments the iron was oxidized, and they scarcely leave a doubt, but that by a partial abstraction of oxygen from carbonic acid, carbonic oxide is formed. It is true, that a portion of water exists in carbonic acid gas; and Berthollet has supposed, that this water, decomposed by the iron, afforded the hydrogen necessary, as he conceives, to the constitution of the gas; but we have no proof that the quantity is such as would furnish any appreciable quantity of hydrogen to enter into the composition of the large quantity of gas obtained. The experiment of passing carbonic acid gas over ignited iron was repeated too by Clement and Desormes, who, in order more completely to abstract the water, had previously exposed the gas to muriate of lime. It was almost totally changed into carbonic oxide; and it is evidently extending the hypothesis too far, to suppose the existence of hydrogen in the carbonic oxide, derived from the water which the carbonic acid, under such circumstances, could contain.

The original experiments of Priestley, in which this gas was procured from a mixture of carbonate of barytes and iron, is perhaps still more incompatible with the opinion that hydrogen exists in the composition of this gas; for allowing that carbonic acid in its gaseous form contains water which might furnish that hydrogen, it is generally admitted by chemists, that native carbonate of barytes contains no sensible quantity of water; and on this is explained the fact, that its carbonic acid is very imperfectly expelled from it by heat, that water not being afforded which is requisite to the constitution of carbonic acid.

How then is it to furnish hydrogen for the formation of carbonic oxide? Were this compound formed only by the intervention of charcoal, the existence of a portion of hydrogen in its composition might be maintained, and would be even the more probable opinion; but its production, from the decomposition of carbonic acid, and especially under these circumstances, without the presence of charcoal, or any substance containing hydrogen, appears to preclude such a supposition.

The inflammable gas obtained from the decomposition of carbonic acid by the metals, so far resembles that produced from the mutual action of charcoal, and the metallic oxides, as to be of the same specific gravity. Like it, too, when mixed with common air, and ignited, it does not explode, but burns slowly, with a blue lambent flame. It requires, however, rather less oxygen for its saturation, and it does not, according to Mr Cruickshank, afford any sensible portion of water in burning, while the other, when burnt in large quantity, deposited moisture on the sides of the vessel. From this circumstance, as well as from the fact established by his experiments, that the weight of the carbonic acid produced in the combustion of this gas, is, as near as can be expected, equal to the weight of the quantity of it consumed, and the quantity of oxygen with which it combines, he infers, that it is a pure oxide of carbon. 100 cubic inches weighing 30 grains, combine in burning with 13.6 grains of oxygen, and afford 43.2 grains of carbonic acid, without any sensible portion of water; whence, on the assumption of the composition of carbonic acid, that it contains one-fifth of pure carbon nearly, he infers this inflammable gas to be composed of 21 of oxygen, and 8.6 of carbon. Thus, according to that assumption, 43.2 of carbonic acid consist of 8.6 carbon, and 34.6 oxygen; but the quantity of oxygen which combined with such a quantity of carbonic oxide as afforded 43.2 of carbonic acid, amounted only to 13.6 grains; whence there remain 21 of oxygen, which that quantity of oxide must have contained.

The nature of this gas is also demonstrated in another experiment, by which a similar conclusion is established,—the action of oxymuriatic acid gas, as shewn by Cruickshank and Guyton. By mixing them together, the oxymuriatic acid gas being in rather more than an equal measure, and allowing the mixture to remain for some hours, the oxymuriatic acid gas parting with oxygen to the carbonic oxide, the latter is entirely converted into carbonic acid.

From the general facts, then, relating to this gas, it appears to be an oxide of carbon. There is one fact, however, rather singular, which is employed by Berthollet as an argument for concluding that it contains hydrogen as an essential ingredient; its specific gravity being less than that of carbonic acid. Pure oxygen gas is heavier than atmospheric air; saturated with carbon, it forms carbonic acid, which has a still greater specific gravity; yet by increasing the proportion of the carbon, a fixed and heavy substance, a compound is supposed to be formed, not only lighter than the carbonic acid, but lighter than the oxygen gas itself. This presents a striking anomaly. According to the proportions given by Clement and Desormes, 48 parts by weight of oxygen, which require only 19 of carbon to form carbonic acid, may hold in solution

52 of carbon, in forming carbonic oxide gas ; and yet this gas shall have a specific gravity, inferior even to that of oxygen gas. " The specific lightness of this gas, (says Berthollet), cannot be reconciled with the supposition, that it consists only of carbon and oxygen, since it requires that the oxygen, after having experienced a contraction in the formation of the carbonic acid, shall follow a course so opposite, that the combination resulting from a much more considerable addition of a solid and scarcely expansive element, will become specifically lighter than that of its elements, which are naturally light, and have a great disposition to elasticity ; while the addition of hydrogen gives a natural explanation of this lightness. Thus this supposition is contrary to every thing which observation teaches us with respect to gaseous combinations, in which there is not one known which acquires less specific gravity than the lightest of its elements, and is subversive of the general principles which are the result of all the chemical facts, since it supposes that the combination is not owing to any attraction, but a repulsion *.

Mr Davy, in answer to this argument, has given a case somewhat analogous, though not perfectly so, where the weight of the compounds resulting from a combination in different proportions is greatest in that which contains the largest proportion of the lighter ingredient. It is that of nitrogen and oxygen, as forming nitrous and nitric oxides. Oxygen is of greater specific gravity than nitrogen ; and yet nitric oxide gas becomes specifically heavier, du-

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* Chemical Statics, vol. ii, p. 81.

ring its conversion into nitrous oxide, by the abstraction of a part of its oxygen *.

The quantity of hydrogen, too, which can be supposed to exist in carbonic oxide, seems too minute to afford a solution of this anomaly, which must therefore be regarded rather as a peculiarity of chemical combination. Even in the gas obtained from the mixture of oxide of zinc and charcoal, and which is not the purest carbonic oxide, the proportion is fixed by Berthollet himself at 1.7 grains of hydrogen in 100 cubic inches. It is difficult to conceive, that so small a quantity should be the counteracting agent to the gravity and fixity of the large proportion of carbon, which carbonic oxide contains above that contained in carbonic acid.

The properties of this gas, farther than what have been stated in the preceding abstract, have scarcely been noticed, except a few of them by Clement and Desormes. Its specific gravity, as stated by Cruickshank, is 1.185, or, compared with atmospheric air, is as 967 to 1000. It is absorbed in small quantity by water, 100 cubic inches of water absorbing 2.01 of the gas. It is fatal to life when inspired. It burns with a blue flame, and does not explode even when previously mixed with atmospheric air, and the electric spark is transmitted through it; nor can the mixture of it with oxymuriatic acid gas be kindled. For its perfect combustion, it is necessary that a considerable excess of oxygen should be present. It affords in burning no sensible portion of water, but is converted into carbonic acid. Clement and Desormes supposed it to

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* Journals of the Royal Institution, vol. i. p. 317.

be decomposed, by passing it with a large quantity of hydrogen through an ignited glass tube, water being formed, and charcoal deposited; but Saussure *junior* shewed this to be a mistake, the appearance of carbonaceous matter being owing to the action of the hydrogen at this temperature, on the oxide of lead of the glass tube. It forms no combination with nitrogen, nor does it act on sulphur even in fusion. It appears to be capable of dissolving a small portion of melted phosphorus. It contracts no union with any of the alkalis, nor is there any reciprocal action between it and the gaseous acids, with the exception of the oxymuriatic, the action of which has been described.

SECT. I.

OF OXYCARBURETTED HYDROGEN GASES.

THE Gases which are the subject of the present section, have been generally regarded as binary compounds of Carbon and Hydrogen in different proportions, and have hence received the specific appellation of Carburetted Hydrogen, the names of the varieties being derived from the substances from which they are obtained. There cannot, however, be the least reason, I believe, to doubt but that they are ternary compounds of carbon, hydrogen, and oxygen; and the name Oxycarburetted Hydrogen, therefore, properly belongs to them. There is scarcely any part of the details of chemistry of more difficult investigation, or more involved in uncertainty, than what relates to these combinations, as their analysis is liable to all those sources of error which we have found to operate in estimating the composition of charcoal, and of carbonic oxide and acid. The results of different experiments are, accordingly, very different; and at present perhaps we are unable to determine the proportions of their elements.

A series of experiments on the analysis of these combinations was made by Dr Austin *, but the state of chemical knowledge at that period did not admit of their being sufficiently accurate and conclusive. It is principally from the experiments of Cruickshank, compared with those of the French chemists, that our conclusions are to be drawn.

Several varieties of these gases exist, having a resemblance in their properties, but capable of being discriminated from each other. They are distinguishable from carbonic oxide gas, by their less specific gravity, by requiring more oxygen to saturate them, and producing less carbonic acid with always a sensible proportion of water.

The one which has been longest known to chemists, is that obtained when water is decomposed by charcoal at the temperature of ignition. It was discovered, or its production and properties first observed, by Dr Priestley, who gave it the name of Heavy Inflammable Air. In the new nomenclature, it was named from its composition, Carbonated Hydrogen, or Hydro-carbonate, a name proposed to be altered by Mr Chenevix, in consequence of his views of chemical nomenclature, to Carburetted Hydrogen. The process by which it is obtained, consists in placing small pieces of charcoal in an earthen or iron tube, which is rais-

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* Philosophical Transactions, vol. lxxx. p. 51.

ed to a red heat by being placed across a furnace, and, either by means of a funnel connected with one extremity of the tube, the aperture of which is nearly closed with a screw, dropping water upon it very slowly, or, what is preferable, distilling water from an earthen retort connected with the tube, so that the vapour shall pass over the ignited charcoal; a quantity of gas issues from the other extremity of the tube, which may be collected over water. The same products are obtained, though in less quantity, by moistening charcoal with water, and exposing it to a strong heat. The theory of the process is, that at the high temperature the water is decomposed by the charcoal, its oxygen combines with one portion of it, forming carbonic acid, its hydrogen with another, forming the carburetted hydrogen gas; the decomposition being owing to these joint affinities of carbon to oxygen and of carbon to hydrogen. The carbonic acid can be abstracted by agitating the gas with water either pure, or still more quickly and effectually with water in which a small quantity of lime is suspended, and the carburetted hydrogen gas remains pure.

With regard to the composition even of this gas, a degree of uncertainty exists. It has been regarded as a binary compound of carbon and hydrogen, the oxygen of the water combining, it was supposed, with one portion of the carbon, and forming carbonic acid, while its hydrogen combines with another portion of the carbon, and forms this species of inflammable gas. But it is obvious, that the supposition is *à priori* equally probable,—that in the process by which it is formed, while one part of the oxygen of the water may combine with a portion of the carbon to form carbonic acid, another portion of it may still pass with the hydrogen into combination with the remaining carbon, and form a ternary compound. There is one fact which favours this conclusion, and even proves that the oxygen of the water enters into the composition of what is named the Carburetted Hydrogen Gas. Mr Cruickshank, in examining the gas disengaged by a red heat from moist charcoal, found, that the first portion consisted of 9 of carbonic acid, and 57 carburetted hydrogen; about the middle of the process it consisted of 3 of carbonic acid with 55 carburetted hydrogen, and the last portions were the latter gas nearly pure. The change in the relative quantities, as the decomposition proceeded, had probably altered the affinities, so that towards the commencement, more of the oxygen had entered into the binary combination with carbon, but towards the end had entered rather into ternary union with the hydrogen and carbon; while if the oxygen of the water enter exclusively into combination with one portion of carbon to form carbonic acid, and the hydrogen likewise exclusively with another portion to form carburetted hydrogen, it is obvious, that while the decomposition went on, or, in other words, in all stages of the process, these two gases should be disengaged in a determinate and invariable proportion.

The composition of this gas has been endeavoured to be determined by analysis, and this establishes the same conclusion. This analysis was performed by Mr Cruickshank, by the agency of the electric spark; a mixture of it with oxygen gas being exploded in a glass tube, the quantity of oxygen consumed by a given weight of it, and the quantities of water and carbonic acid formed, being ascertained. 100 cubic inches of it weighing 14.5 grains, mixed with oxygen gas, and exploded over mercury, required for saturation, 66 cubic inches, or 22.4 grains. 40 cubic inches of carbonic acid, weighing 19 grains, were produced; the quantity of water deposited was estimated at 9 grains, and the quantity held in solution likewise at 9 grains. From these facts, and assuming the common calculations with regard to the composition of water and carbonic acid, Mr Cruickshank inferred that the inflammable gas obtained from wet charcoal by a strong heat, consists of 4 of carbon, 1.3 hydrogen, and 9 water. This, however, involves a hypothetical assumption, that the whole or any considerable part of the water pre-existed in the gas ready formed. It is equally possible *à priori*, that the elements of this water, the oxygen and hydrogen, may have been in immediate combination with the carbon of the gas, and with the proportion of hydrogen which Mr Cruickshank assigns; for on this hypothesis, are equally explained, the proportion observed, between the quantity of oxygen consumed, and the quantity of carbonic acid and water obtained from the combustion. And this is much more probable, than that the gas should hold so large a quantity of water in a combined state.

If these views be just, this gas cannot be regarded as a pure carburetted hydrogen, or binary compound of carbon and hydrogen, but as a ternary compound of these principles with oxygen. Such, however, is the difficulty of the investigation, that from the facts at present known, the proportions cannot be accurately fixed.

Berthollet, too, has made this gas the subject of experiments, but with results so different as to render them doubtful; 100 measures, according to his statement, require 70 of oxygen, and produce 28 of carbonic acid. His conclusion is, that it consists of 5 parts by weight of carbon and 4 of hydrogen *.

The specific gravity of this variety of carburetted hydrogen is much greater than that of pure hydrogen gas, being to that of atmospheric air as 11 to 23. According to Mr Cruickshank's estimate, 100 cubic inches of it weigh 14.5 grains. It is insipid, and nearly inodorous. Though inflammable, its inflammability is less than that of pure hydrogen, which adds to the probability of its containing oxygen; when kindled, it burns with a blue lambent flame; 100 measures of it combine in burning, as has been already stated, with 66 of oxygen. During its combustion, a considerable quantity of water is deposited on the sides of the vessel, and the residual gas is carbonic acid.

This gas is eminently fatal to animal life. Breathed pure, it occasions immediate death, and when diluted with 20 parts of atmospheric air, its effects are strongly depressing; it reduces the force of the circulation, causes nausea and vertigo, and if breathed too long, suspension of the vital functions—effects probably owing to its chemical action on the blood. A singular fact, exemplifying this action, has been taken notice of by Dr Beddoes, that venous blood exposed to it assumes a vivid florid hue, similar to that of blood in the arterial state.

In the decomposition of certain vegetable products by heat, other species of carburetted hydrogen are obtained, differing little from the preceding one in their properties,

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* Mémoires de l'Institut National, t. iv. p. 306.

but varying somewhat in their composition, at least as to the proportions of their elements, and containing in particular more carbon. The one which appears to contain least oxygen, is that obtained by passing the vapour of camphor through a red-hot tube. It is considerably heavier than that from wet charcoal, 100 cubic inches under a mean pressure and temperature weighing 21 grains. It requires more than double the quantity of oxygen to saturate it, which the preceding gas does, 100 measures combining with 176 of oxygen gas; this gives as the products, according to Mr Cruickshank's experiments, 116 measures of carbonic acid gas, weighing 54.5 grains, 18 grains of water deposited, and 8 or 9 which he supposes to have been held in solution in the gas; whence he infers that this gas consists of 11 carbon, 2 hydrogen, and 8 or 9 of water.

The associated Dutch Chemists observed, that by passing the vapour of alkohol or of ether through an ignited glass tube, gases are formed, analogous in properties and composition to the preceding varieties of carburetted hydrogen *. Both are rather lighter than that from camphor. That from alkohol they state to have a specific gravity to that of atmospheric air, as 0.436 to 1000; according to Mr Cruickshank, it is in the proportion of 12 to 23. It burns with a pale blue flame, similar to that of alkohol itself. Its analysis was performed by Mr Cruickshank; 100 cubic inches which weigh 16 grains, combine when exploded with oxygen with 118 of that gas, and afford 75 measures of carbonic acid, or 36 grains, 13

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* Nicholson's Journal, 4to, vol. i. p. 52.

of water produced, and 7 held in solution in the gas. In conformity to his usual deductions from such analysis, he concludes that it consists of 7 of carbon, 1.9 of hydrogen, and 7 of water. The results of Berthollet's analysis of it are different; 100 measures, weighing, as he states it, 20 grains, require 140 measures of oxygen gas, 90 of carbonic acid, being produced, whence he supposes it to consist of 15 carbon and 5 hydrogen *. The gas obtained by passing the vapour of sulphuric ether through an ignited tube, is, according to the Dutch Chemists, heavier than that from alkohol, its specific gravity being to that of atmospheric air as 6.709 to 1000,—a distinction between them which Mr Cruickshank also observed, the specific gravity of the one, that from alkohol, according to him, being to that of atmospheric air as 12 to 23; of the other, that from ether, only as 15 to 23. It burns with a more dense and oily like flame, of a blue colour, and requires for its saturation a much greater quantity of oxygen; 100 cubic inches, which weigh 20 grains, combine with 170 of oxygen gas, or 58 grains, affording 108 cubic inches, or 50.5 grains of carbonic acid, 18 of water, besides 9, which it previously held in solution, whence Mr Cruickshank infers it to consist of 9 of carbon, 3 of hydrogen, and 8 of water. It is the medium compound, therefore, between the gas from camphor and that from alkohol. It is scarcely necessary to remark, with regard to the inference of Mr Cruickshank, as to the quantity of water which he supposes to exist ready formed in these gases, that the same objection applies to it as to the same inference with

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* Mémoires de l'Institut National, t. iv. p. 301.

regard to the gas, obtained at a red heat from moistened charcoal. We have no proof whether the water, or only the elements of the water, exist in the gas; and the conclusion is more probable that these gases are ternary compounds of carbon, hydrogen, and oxygen, than binary compounds of carbon and hydrogen, holding large quantities of water dissolved.

Mr Cruickshank observed, that the gas which arises from marshes, disengaged, no doubt, from the slow decomposition of humid vegetable matter, is similar to the gases obtained from the decomposition of camphor, or ether, by heat. According to Mr Dalton, it is contaminated with about 20 *per cent.* of nitrogen gas. Dr Henry has found, that the gas which arises from coal mines, and is known by the name of Fire Damp among the miners, is of a similar nature, containing a small intermixture of carbonic acid gas, and a larger portion of atmospheric air*.

All these varieties of carburetted hydrogen gases, as they have been named, are capable of being analysed from the operation of another chemical agent upon them; the oxymuriatic acid gas. It parts with a large quantity of oxygen with great facility, and therefore if mixed with these gases in due proportion, and allowed to stand for some hours, it converts them into water and carbonic acid with variable quantities of the gas, which has been considered as carbonic oxide. If, instead of allowing the mixture to remain at rest, the electric spark be taken through it, an explosion not violent takes place, with a production of carbonic acid and water, and in the gases from ether and camphor, if a certain proportion of oxymuriatic acid gas has been used, with a deposition of charcoal *. The carbonic oxide gas, mixed with oxymuriatic acid gas, cannot be exploded or inflamed by the electric spark; and this, Mr Cruickshank observes, affords a distinction between it and the above described gases.

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* Nicholson's Journal, vol. xix. p. 149.

The Dutch Chemists discovered a gas belonging to the same family, which is possessed of some very peculiar properties, particularly that of affording oil when acted on by oxymuriatic acid gas, whence it has received the name of Olefiant Gas. When alkohol is mixed with an equal weight of sulphuric acid, and exposed to heat, the product named Sulphuric Ether is formed. These chemists observed, that, at a certain stage of this process, or towards the end of the formation of ether, this gas is produced, and by taking the proportions of acid and alkohol which exist at this period, consisting of from 3 to 4 of concentrated sulphuric acid to 1 of alkohol, it may be produced in abundance without ether. The alkohol is put into a retort, and the acid poured upon it; on mixing them by agitation, the fluid becomes warm, and acquires a brown colour; gas begins to be disengaged, the formation and disengagement of which is accelerated by applying a moderate heat. It is received over water, and consists of sulphurous acid mixed with olefiant gas; the former is abstracted by agitation, either with pure water, or, still better, water to which a little lime or ammonia has been added. The olefiant gas is then obtained pure †.

This gas, from the nature of the process in which it is

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* Nicholson's Journal, 4to, vol. v. p. 202. † Ibid. v. i. p. 44.

obtained, may be inferred to be a compound somewhat similar to the gases already described. The presence of carbon and hydrogen is apparent from the production of water and carbonic acid in its combustion, and is farther proved by transmitting it over sulphur in fusion, when sulphuretted hydrogen is formed, and carbon deposited. The discoverers of it infer that it contains no oxygen, but without any sufficient proof; and the presence of this principle appears to be established by the result of the transmission of the gas through an ignited porcelain tube, when, according to the Dutch Chemists, carbonic acid is formed. This, however, has been denied by Berthollet. It does not appear to contain any sulphur or sulphurous acid derived from the acid employed in its formation. They endeavoured to determine the composition as well of this gas, as of those obtained by passing ether and alkohol through an ignited glass tube. From the combustion of these with a given quantity of oxygen, they inferred their composition to be nearly the same,—from 80 to 74 of carbon, with from 20 to 26 of hydrogen, the oily gas containing the largest proportion of carbon, and that from alkohol decomposed in a glass tube, the least *. The younger Saussure, in his researches on the composition of alkohol and ether, submitted to analysis the gases obtained by passing these liquids through an ignited tube glazed internally. That from the decomposition of alkohol, he concludes, consists of carbon 52.9, oxygen 27.2, hydrogen 15.6, and nitrogen 4.3. That from sulphuric ether decomposed by the same process, is composed of carbon

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* Nicholson's Journal, 4to, vol. i. p. 52.

56.12, hydrogen 17.43, and oxygen 26.45. He observes, however, what renders all such analyses of little direct value, that nothing is more variable than the composition of these gases, according to the degree of heat, the diameter of the tube, and the period of the experiment at which they are collected *.

Berthollet endeavoured to determine the composition of olefiant gas with more precision. In combining it by the electric spark with oxygen gas, he found that 100 parts required 280 by measure, and produced 180 of carbonic acid, whence he inferred it to consist of 75 carbon and 25 hydrogen †. Mr Henry, in a subsequent series of experiments, found that the olefiant gas required for its saturation the largest quantity of oxygen of any variety of what has been named carburetted hydrogen, 100 measures requiring 284; while the same quantity of pure hydrogen required only from 50 to 54, and of gas from moistened charcoal only 60. This proves, therefore, that a given volume of olefiant gas contains more inflammable matter than any other of these gases do; and that much of this is carbon, is evident from the large quantity of carbonic acid produced in its combustion, 100 measures, according to Mr Henry, giving 179. In a latter memoir, he has stated the quantities even higher, 100 cubic inches of olefiant gas consuming 325 of oxygen, and producing 200 of carbonic acid.

Berthollet found, that when an inferior proportion of oxygen is used, as three measures with four of the olefiant

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* Nicholson's Journal, vol. xxi. p. 269. 326.

† Mémoires de l'Institut National, t. iv. p. 296.

gas, the combustion is feeble, a little water is formed, and some charcoal deposited. But, instead of being a diminution, there is a considerable increase of volume, and the aëriform fluid thus produced, he regarded as a ternary combination of the greater part of the oxygen with the elements of the olefiant gas, *minus* the small quantities of hydrogen spent in the formation of the water and of the charcoal deposited.

The specific gravity of this gas is much greater than that of the other gases of this genus, being to that of atmospheric air as 909 to 1000. Its odour is slightly fœtid; it is not absorbed or altered by contact with water; Mr Dalton affirms, however, that it suffers a sensible absorption; it burns with a strong dense oily like flame, and when previously mixed with oxygen, and a spark sent through the mixture, detonates with great violence. Very few chemical agents exert any sensible action on it; by the electric spark continued to be taken in it for some time, it is changed in its chemical properties without any diminution in its volume, owing apparently to part of its oxygen and carbon being combined so as to form carbonic acid.

There is one chemical agent, however, the oxymuriatic acid, which exerts upon it a singular action, changes its composition, and condenses it into a liquid, having all the properties of oil. If equal parts of the two gases are mixed over water, a condensation takes place quickly with an evolution of heat, and this oily like matter condenses on the sides of the vessel, and on the surface of the water. If 4 parts of the oxymuriatic acid gas and three of the inflammable gas be mixed together, the condensation is complete, any residual gas being only nitrogen or carbonic acid, which may have been accidentally mixed with the gases. If the gases, immediately on their mixture, be kindled, the combustion is attended with smoke, and a deposition of charcoal on the sides of the vessel.

The oily matter formed by the action of these gases, gradually collects into globules, which at length sink through the water. It is whitish and semi-transparent, has a perceptible smell, which is not disagreeable, and a sweetish taste. By agitation it may be dissolved in water.

The production of this substance is not sufficiently elucidated. It depends on the oxymuriatic acid gas parting with its oxygen, but it is uncertain whether the oxygen combines with the entire principles of the olefiant gas to form the oil, or whether it unites only with a portion of the hydrogen of the gas, and forms water, the remaining elements, in the proportion in which they are thus left, forming oil. It appears that the production of the oil from this species of gas depends principally on the condensation of its principles, and the large proportion of carbon, since, when transmitted through an ignited porcelain tube, it is converted into an inflammable gas, which is much more rare, and does not afford oil when acted on by the oxymuriatic acid; and at the same time a large quantity of carbon is deposited, and carbonic acid formed *.

The Dutch Chemists found that the olefiant gas is produced, though not perfectly pure, in some other processes besides that above described, and they observed some singular facts with regard to its production. Thus it is formed by passing the vapour of alkohol, or of ether, through

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* Nicholson's Journal, 4to, vol. i. p. 54.

an ignited tube of pipe clay, while it is not formed in an ignited glass tube, the gas produced in the latter experiment, though inflammable, not affording oil from the action of oxymuriatic acid. If, in the glass tube, however, a quantity of silex or argil be put, on raising it to a red heat, and passing the vapour either of alkohol or ether over it, there is a production of olefiant gas. The same effect is not obtained when lime or magnesia has been put into the glass tube, a gas of a different nature being formed. The precise explanation of these apparently anomalous facts is difficult, but the effects depend probably on the different powers of the different substances of communicating temperature; a slight variation in the temperature, communicated to the vapour in its rapid passage through the tube, varying the affinities of its elements, and determining their combination in various proportions.

A gas of a similar nature appears to be produced in the decomposition of wood and other vegetable substances by heat. It is known that in that decomposition a quantity of oil is produced even where the substance decomposed is not in the least of an oily nature; and the inflammable gas which is also disengaged, burns with a dense oily-like flame, and deposites even a quantity of charcoal if the supply of air be not very rapid and abundant.

It appears also, that the gas which has lately been procured from coal by the application of heat, and applied to the purpose of obtaining artificial light, is analogous to these latter gases. It burns with a very dense oily-like flame, and a given quantity of it produces much more illumination than pure hydrogen gas, or the carburetted hydrogen obtained in the decomposition of water by charcoal, no doubt owing to the condensation of its elements, in consequence of which a larger quantity of inflammable matter is contained in a given volume of gas; and accordingly Dr Henry has found, that in the combustion of this gas more oxygen is consumed than in that of the other gases, the quantity being inferior only to that which is required in the combustion of the pure olefiant gas, and in that of the gases which are obtained from the decomposition of oil and wax by heat. It might be supposed to consist of the olefiant gas itself, more or less mixed with other aëriform fluids. That there is such an intermixture appears from Dr Henry's experiments on this gas *; it contains carbonic acid, sulphuretted hydrogen, and a portion of olefiant gas; but by far the greater part of it, amounting generally to 90 or more in 100 parts, is a peculiar gas, which has not the properties of the olefiant gas, and which is not easily reduced to any known species. It varies, too, as obtained from different coals, and even at different stages of the process. Its application to the purpose of procuring illumination will be noticed under the history of coal.

The gases which are obtained from oil and wax resemble the gas from coal, and the pure olefiant gas in the great illumination produced by their combustion, arising no doubt from the same cause, the condensation of their elements, and in consequence of which, as their constituent principles are chiefly carbon and hydrogen, a given volume of gas contains a large portion of inflammable matter. There can be no doubt but that these gases are produced in the combustion of oil, tallow, and wax, the

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* Philosophical Transactions, 1808.

heat present in the wick in the burning of these substances for obtaining artificial light decomposing the unctuous matter and forming the gas; the combustibility of which, or rather the quantity of light afforded by its combustion, is also probably increased by a portion of oily matter in vapour mixed with the gas.

There have thus been described, a number of gases composed of carbon, hydrogen, and oxygen united in various proportions, and by multiplying experiments and examining the gases evolved in the decomposition by heat of different vegetable substances, it is by no means unlikely that the number may be augmented and others be discovered, varying in the proportions of their principles. Carbon, hydrogen, and oxygen, are principles, the affinities of which are so much alike in force as to be capable of being balanced in almost indefinite proportions. In the vegetable kingdom, an immense number of products are formed from their combination, and there appears some reason to believe that, though those formed by art must be less numerous, yet they are probably not limited merely to a few determinate proportions, but may be much varied even by slight variations of circumstances.

It appears probable too, as Mr Henry has remarked *, that these gases are disengaged in the processes by which they are formed not unfrequently in a state of mixture, by which, trusting to their analysis alone, their number might be unnecessarily multiplied, as what from the products of its combustion might be regarded as a distinct gas, may be only a mixture of others. In proof of this, Dr Henry

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* Nicholson's Journal, vol. xi. p. 70.

has adduced the fact observed by Mr Cruickshank, but not explained by him, that some of what he regarded as carburetted hydrogen gases, afforded different quantities of carbonic acid in burning, according as they had been previously washed with water or not, although the original gas contained no carbonic acid whatever. It can scarcely be supposed that the weak affinity of water could determine the combination of the elements of the gas in any new proportion, so as to form a portion of a soluble compound. It must rather be imagined, that it had been a mixture, containing part of a gas more easily absorbed than the residual part. Olefiant gas, Dr Henry accordingly remarks, is more absorbed by water than any of the other gases of this family; and hence the above difference is probably owing to its presence in the gas, and its removal by the washing. The fact, that some of these gases by admixture of oxymuriatic acid, quickly undergo a partial diminution of volume, is less conclusive, as this gas, by its more powerful affinity, may determine the formation of a portion of olefiant gas, the formation proceeding rapidly until put a stop to by the change of proportions which it occasions.

Dr Henry and Mr Dalton have supposed, that all these gases may be reduced to two species, what has been named Carburetted Hydrogen being the gas obtained in the decomposition of water by charcoal, and Olefiant Gas; these, mixed in various proportions, and frequently with portions of carbonic acid, carbonic oxide, and of pure hydrogen, constituting the different aërial fluids obtained in the decomposition of vegetable substances by heat.

These opinions are in some measure opposed to each other; and it is not easy to determine which is just. It is no doubt sufficiently probable, that in the decomposition of a ternary compound of carbon, hydrogen, and oxygen, more than one new combination may be established, from the difficulty of rendering the circumstances uniform through the whole mass; and that hence different elastic fluids may be evolved together. But it is equally probable, from the general views of chemical theory, that these elements may combine in numerous proportions, and may thus form a number of compound elastic fluids. There are no facts on the subject inconsistent with this supposition. And it would not be easy, perhaps, to reduce all the aëriform products of these processes to mixtures of the species Dr Henry and Mr Dalton have assumed.

While there is no subject in the details of chemistry of more difficult investigation than what relates to the composition of these gases, there is none of more importance, for on it is immediately dependent the accuracy of vegetable analysis. In general, the analysis of a vegetable product can be performed only by decomposing it by heat; and in this process, its carbon, hydrogen, and oxygen, are disengaged in new combinations generally aëriform; from an accurate knowledge of which, therefore, only can a just inference be made as to the composition of the vegetable matter; and with regard to this, all our conclusions must be uncertain while our knowledge of these combinations is in its present imperfect state.

Since these gases probably vary in their composition according to circumstances, and are probably also frequently disengaged in a variable state of mixture, it would be in vain to seek to establish our conclusions by fixing the composition of certain gases which are distinguished by characters sufficiently specific, and then discovering what proportions of these gases are evolved in our analysis; for we shall be perpetually exposed to error from variations in composition or admixture, by slight changes of circumstances. The only mode on which reliance can be placed, will be that of subjecting to analysis the products of each process; and with regard, therefore, to the inflammable gases, the great desideratum is a mode accurate, and not difficult, of determining their composition. The vegetable analysis, so far as connected with the most important part of it, the determination of the nature of the gaseous products, would then resolve itself into two steps: 1st, As there will be generally evolved a quantity of carbonic acid gas, to separate it from the inflammable gas; and, 2dly, By an immediate experiment, to determine what quantity of carbon, hydrogen, and oxygen, a given volume of the residual inflammable gas contains. This important problem has engaged the attention of Dr Henry, and he has given the most accurate process by which this analysis may be executed.

The analysis has been performed by detonating a mixture of the inflammable gas with a known quantity of oxygen gas in a tube, by the agency of the electric spark; after the detonation the diminution of volume is ascertained: the quantity of carbonic acid which has been produced is then determined by its absorption by an alkaline solution or lime-water; then the quantity of oxygen which remains is discovered by a eudiometrical process, and of course the quantity is discovered which had been consumed. We thus arrive at the determination of the quantity of carbon that had been contained in the gas; and from the consumption of oxygen beyond that which is necessary to convert this into carbonic acid, we infer what quantity had gone to the formation of water, and of course what quantity of hydrogen the gas had contained, the calculation for this being facilitated by the assumption of what appears now to be sufficiently established, that oxygen gas in being converted into carbonic acid gas suffers no change of volume. This will be illustrated from the following table given by Dr Henry, exhibiting the results of his experiments on these gases.

Kind of Gas.	Oxygen Gas required to saturate 100 Measures.	Carbonic Acid produced.
Pure hydrogen,	50 to 54	
Gas from moist charcoal,	60	35
——— wood (oak)	54	33
——— dried peat,	68	43
——— coal, or cannel,	170	100
——— lamp oil,	190	124
——— wax,	220	137
Pure olefiant gas,	284	179

"If it be assumed," adds Mr Henry, "that in the formation of each measure of carbonic acid, in the above experiments, an equal volume of oxygen gas is employed, we shall learn, by deducting the numbers in the third column from the corresponding one in the second, what proportion of the consumed oxygen has been allotted to the saturation of the hydrogen of each hydro-carburet. Thus, for example, in the combustion of the gas from coal, 70 parts of oxygen have disappeared, besides that which has entered into the carbonic acid; and, since each measure of oxygen saturates two of hydrogen gas, the gas from coal must contain, in 100 measures, a quantity of hydrogen which, expanded to its usual elasticity, would occupy 140 measures. By a similar mode of estimation, the quantity of hydrogen in other species of inflammable gas may be ascertained, viz. by subtracting the number in the third from the corresponding one in the second column, in each instance, and doubling the remainder *."

Dr Henry has found, however, that in the method by detonation, there are sources of error which render the results uncertain; so that the products of the combustion of the same gas varied in different experiments; and the quantity of gas operated on being necessarily small, these errors become more important. He has therefore proposed another, in which a stream of the inflammable gas is made to burn in oxygen gas; a larger quantity can thus be operated on; and the quantities of oxygen gas consumed, and of inflammable gas burned, can, by the nature of the apparatus, be accurately ascertained. One farther step indeed is necessary; for during the burning it appears that part of the inflammable gas escapes unconsumed, and mingles with the residual air. The quantity of this therefore requires to be ascertained, which is done, by rendering the mixture of it with the residual oxygen capable of detonating by the addition of a known volume of pure hydrogen, and ascertaining the consumption of oxygen in this detonation, and the products †.

From the scale on which the experiment can thus be performed, it must be liable to less uncertainty than the method by detonation. The deductions too are now in some measure rendered more satisfactory, from the pro-

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* Nicholson's Journal, vol. xi. p. 66.

† Philosophical Transactions, 1808.

portions of the elements of carbonic acid being now astained with more certainty. But there still remains one source of uncertainty, probably more difficult to obviate,—that with regard to the quantity of water which these gases may hold dissolved. The analysis may indicate, that a certain portion of hydrogen and oxygen exists in the inflammable gas; but what portion of these is in simultaneous combination with its elements, and what in the state of water, is not known; nor is it easy to determine the quantity of water which the carbonic acid gas may hold combined, and thus disguise. Hence some chemists, as has been already remarked, have inferred, that these gases are binary compounds of carbon and hydrogen, holding water in solution. The opposite conclusion, that they are ternary compounds of carbon, hydrogen and oxygen, is much more probable; but, as even on this hypothesis, a small portion of water may exist in the gases themselves, or in the carbonic acid produced, it renders difficult the determination of the exact proportions of the elements. Hence the importance of the question with regard to the existence of combined water in aëriform fluids. Its relation to the present subject is more particularly considered in the discussion of that question, to which I refer. Note E.

In concluding the history of these aëriform fluids, I may give the table of Cruickshank, which points out the principal facts with regard to their analysis. The results, it will be obvious from the preceding history of these compounds, cannot be regarded as perfectly accurate; and the reader will be aware of the fallacy of the conclusion with regard to the quantities of water supposed to be held in solution by the different gases.

Gases, and the substances from which the gases are obtained, &c. &c.	Weight of 100 cubic inches or measures	Proportion of oxygen necessary to saturate 100 measures of the gas		Products when combined with oxygen.				Hence the gases consist of			
				Carbonic acid.		Water produc	Water held in solution by the gas	Oxygen	Carbon	Hydrogen	Water
				in volume	in quant						
	Grains	Measures	Quantity Grains	Measures	Grains	Grains	Grains				
Pure hydro-carbonate from camphor, &c.	21.	176.	59.8	116.	54.5	18.	8. or 9.	none	11.	2+	8 or 9.
Ditto from ether	20.	170.	58.	108.	50.5	18.	9.	none	9.	3.	8.
Hydrogen from alkohol	16.	118.	40.	75.	36.	13.	7.	none	7.	1.9	7.
Ditto from wet charcoal	14.5	66.	22.4	40.	19.	9.	9.	none.	4 nearly	1.3	9.
Gaseous Oxides,											
from charcoal and metallic oxides	30.	44.	15.	76.	35.5	about 8.	probably none	about 15.	7.	1+	uncertain
Do. from iron filings and carbonate of lime, or barytes	30.	40.	13.6	92.	43.2	none	none	21. +	8.6	none	none

In the preceding table, the weight of 100 cubic inches of common air, under the mean pressure of the atmosphere, and at the temperature of 55°, is estimated at 31 grains; the quantity of pure carbon in carbonic acid at ⅕ of the whole nearly, and the proportion of oxygen to hydrogen in water as 85 to 15.

CHAP. IV.

OF PHOSPHORIC ACID, AND ITS BASE.

THIS acid, though it exists in the mineral kingdom, in combination with certain metals and earths, is more peculiarly a product of the animal system. Combined with lime it forms the basis of bones; and it exists also in several of the secretions. It was made known to chemists, not by being procured in its insulated form from any of these combinations, but rather in an indirect mode. It was known even to some of the earlier alchemists, that from some varieties of animal matter, a substance could be procured by certain processes, so highly inflammable as to burn from mere exposure to the air. This is the substance named Phosphorus. By the researches of modern chemists it was discovered, that in the processes by which it had been obtained, it was always derived from the decomposition of phosphoric acid; and thus the existence of this acid and its relation to phosphorus were established. The base combines with another proportion of oxygen, forming what has been named Phosphorus Acid. It also unites with hydrogen and sulphur, and several of the alkalis and earths and their bases. We have first, then, to consider the chemical properties of the base itself, and, afterwards, those of these compounds.

SECT. I.

OF PHOSPHORUS.

THIS substance, the base of phosphoric acid, must have for ever remained unknown but for the researches of chemistry. As it combines spontaneously with oxygen, at the lowest natural temperature, it cannot exist pure in nature, and there is even considerable difficulty in obtaining it from any of its combinations. There appears reason, from the enigmatical expressions of some of the earlier alchemists, to believe that it was known to them. Brandt, however, an alchemist of the 15th century, is regarded as the proper discoverer of it. He kept secret the method of procuring it. Kunckel, another German chemist, informed of Brandt's discovery, and knowing only that the phosphorus had been obtained from urine, entered on the investigation, and succeeded in discovering the process. It appears, also, to have been known to Boyle. Such however was the difficulty of preparing it, that the process was for a long while attempted by few chemists, and as this substance was an object of much curiosity, from burning slowly, with the emission of considerable light but of scarcely any heat, when exposed to the atmosphere, it bore a high price. Subsequent researches have discovered methods of obtaining it with more facility, though the process is still complicated and difficult.

It is always procured from phosphoric acid, by exposing this to heat with carbonaceous matter, which attracts its oxygen, and allows the phosphorus to be volatilized by the heat applied. This acid, though it exists in the mineral kingdom, occurs principally in the varieties of animal matter, and it is from these that it is always procured for the preparation of phosphorus.

It exists in considerable quantity in urine, being secreted in combination with ammonia, with soda and lime, and it was from this fluid that it was always obtained by the earlier chemists. The essential steps of the process appear to have consisted in obtaining by evaporation these salts, mixed with the extractive matter of the urine. This was subjected to distillation in close earthen-ware retorts, capable of sustaining a very strong fire. The carbonaceous matter present attracted the oxygen of the phosphoric acid, and a small portion of phosphorus was volatilized by the strong heat applied. A considerable improvement was made in the process, by adding a portion of charcoal powder previous to the distillation, by which the phosphoric acid was with more certainty and more completely decomposed. Another improvement made by Margraaf, consisted in adding likewise a portion of muriate of lead, by which the product was increased. The quantity of phosphoric acid combined with the soda and the lime, being united by too strong an affinity to these bases, to admit of being decomposed by the charcoal, it was only the portion combined with the ammonia that underwent this decomposition. The muriate of lead decomposes the phosphates of soda and lime, by attracting the phosphoric acid, and thus facilitates its decomposition by the charcoal.

Still the process was offensive and troublesome, until

Scheele, by discovering that the phosphoric acid exists in bones, gave one less so, and which with some variations is now followed in the preparation of phosphorus.

The bones of animals are burnt to whiteness in an open fire. This white matter, of an earthy-like appearance, consists of phosphate of lime, with a small quantity of carbonate of lime. It is reduced to a coarse powder, is diffused in ten times its weight of water, and half its weight of sulphuric acid is added to it in an earthen vessel; the mixture is kept in a moderate heat, as by the side of a common fire, for 12 or 24 hours, stirring it occasionally, and adding water, as may be necessary, to preserve it soft. At the end of that time, it is placed on a filtre of cloth, and boiling water is poured upon it, until, in filtrating through the mass, it ceases to acquire acidity.

The acid liquor which is thus procured, was supposed to be pure phosphoric acid, separated from its combination with the lime, by the superior affinity of the sulphuric acid; it was observed, however, that on adding an alkali to it, a copious precipitation takes place, the precipitate consisting, as Vauquelin found, of neutral phosphate of lime; the liquor obtained, therefore, is a solution of super-phosphate of lime. The proper theory of the process, in conformity to the principles of affinity already explained, is, that when the phosphate of lime is acted on by the sulphuric acid, the lime is divided between the two acids, in proportion to their respective forces of affinity, and their quantities. The sulphuric acid acquires one portion, the phosphoric acid still retains another. The sulphate of lime, such as is formed with the above proportions, is comparatively insoluble; the super-phosphate of lime is more soluble, and by washing with water it is separated from the undissolved matter.

In the farther steps of the process, the acidulous liquor thus obtained is evaporated (according to Pelletier's recommendation, in a bason of copper) to dryness, and the dry mass was even by some chemists fused by the application of heat. To this solid matter reduced to powder is added half its weight of charcoal powder, and the mixture being put into a coated earthen retort placed in a naked fire, and having a long tube adapted to it, which terminates in a vessel of water, the extremity being nearly immersed in the water, the heat is raised sufficiently to enable the charcoal to attract the oxygen of the phosphoric acid, and to volatilize or distil over the phosphorus, which condenses in part in the tube, and is partly received in the water. The quantity obtained varies according as the operation is skilfully conducted. Pelletier states, that by one distillation he had often obtained 60 ounces of phosphorus, 30 pounds of sulphuric acid, and 36 pounds of calcined bones having been used *, and at other times not more than 30 ounces.

Though the quantity may be considerable, a loss is sustained in consequence of the lime present, by its affinity to the phosphoric acid preventing a portion of it (not less, according to Vauquelin, than one half of the quantity present) from being decomposed by the charcoal. Different additions have been made to remove or obviate this; and Vauquelin, adopting the improvement originally suggested by Margraaff, added to the super-phosphate of lime ob-

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* Mémoires de Chimie, t. i. p. 252. 284.

tained by washing the mixture of burnt bones and sulphuric acid, a quantity of acetite, (or, what there is reason to believe is preferable, nitrate of lead), the oxide of lead combines with the whole phosphoric acid, and forms an insoluble precipitate; this phosphate of lead is then washed with water, dried, mixed with half its weight of charcoal, and exposed to heat as in the preceding process. But although in this way the whole of the phosphoric acid, or nearly the whole, is decomposed by the charcoal, it may be doubted whether there is not a considerable loss of phosphorus by the combination it forms with the lead, which is at the same time reduced to the metallic state.

This has been proposed to be remedied, by previously decomposing the phosphate of lead, by muriatic or sulphuric acid, which it has been supposed combines with the oxide of lead, and allows the phosphoric acid to be disengaged. This, however, renders the process more complicated, nor will probably even all the phosphoric acid be thus obtained. The best method appears to be that pointed out by Dr Higgins *, adding to the super-phosphate of lime, carbonate of ammonia, so as to produce perfect neutralization. The carbonic acid combining with the lime, the greater part of the phosphoric acid is united with the ammonia; this phosphate of ammonia remains dissolved, while the carbonate of lime is precipitated; the solution is poured off, is evaporated until it become solid, is then urged with a red heat in a thin glass vessel; the greater part of the ammonia is expelled, the phosphoric acid, nearly pure, remains in a vitrified state; it is reduc-

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* Minutes of a Philosophical Society.

ed to powder, mixed with half its weight of charcoal; and when exposed to a sufficient heat, affords by distillation about one-fourth of its weight of phosphorus. This process has the advantage, too, that the phosphorus is obtained purer, and in particular free from any sulphur, with which, in the other modes, it is liable to be contaminated, from part of the sulphuric acid employed in the decomposition of the burnt bones being retained in the subsequent steps; while in this it is expelled in combination with the ammonia, from the phosphoric acid.

The distillation of the phosphorus, according to any of these methods, requires considerable care. The principal circumstances have been pointed out by Dr Higgins. The earthen retorts to be met with in this country, are so porous at a high temperature, that a great part of the phosphorus is lost; the retort used, therefore, ought to be previously washed externally with a strong solution of two parts of borax mixed with one of lime, which during the incandescence forms a glazing that renders it impervious. By being farther coated with clay and sand, it is less liable to injury from any sudden alteration of temperature. The retort should have a wide neck, and the tube connected with it, which dips a little in water, should be equally wide, that the phosphorus, in distilling over, may not, by congealing in it, so far close the aperture that the elastic fluid, consisting of carbonic oxide and acid holding a little phosphorus dissolved, which is disengaged copiously, shall not escape freely, by which the retort would be burst. When from the diminution in the size of the bubbles of air which escape, there is any reason to fear this, a hot iron ought to be applied to the tube to melt any phosphorus. A portion of the gas disengaged during the distillation, ought to be collected and introduced into the neck of the retort as it cools, at the end of the process, to prevent the water from passing back, as atmospheric air admitted for that purpose would kindle the film of warm phosphorus in the tube.

The phosphorus obtained by the first distillation is not pure. It is of a dark brown colour, and not transparent, from the presence of a quantity of carbonaceous matter. Different methods have been practised to purify it. Distillation succeeds, though it is somewhat difficult, from the risk of the first portion of phosphoric vapour taking fire from the action of the air of the retort. The method Dr Higgins employed, was to put the phosphorus into a widé-necked retort, which was filled with water; the retort was heated until the phosphorus had melted, and when cold, adhered to the bottom of the retort; the water was then displaced by introducing hydrogen gas; and the retort being placed in sand, the extremity of the neck still remaining immersed in water, the phosphorus, by the application of heat, was distilled over, and was thus obtained colourless and transparent [*]. Another method which has been followed, is to digest the phosphorus obtained by the first distillation, with nitrous acid, or, as Mussin Puschin recommended, with nitromuriatic, or oxymuriatic acid [†]; any of which, by oxidizing the carbonaceous matter, renders the phosphorus quite colourless and pure. The mode of applying the oxymuriatic acid described by

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[*] Minutes of a Society for Philosophical Exper. p. 261.

[†] Annales de Chimie, tom. xxv. p. 102.

Trommsdorff, consists in melting phosphorus in boiling water, and agitating it as the water cools, that it may be reduced to powder, then pouring on this powder a little diluted oxymuriatic acid for a few minutes. The phosphorus, when again melted, is perfectly colourless. According to Pelletier, however, the nitrous acid (and the oxymuriatic will have probably the same effect) oxidizes a portion of the phosphorus, and renders it less inflammable. The simplest method, is one suggested by Woulfe and recommended by Pelletier [*]. It is merely straining the phosphorus through fine chamoy leather. The impure phosphorus is put into a piece of leather of this kind, tying it in the form of a bag, and covering it with cold water. It is then put into boiling water, and when the phosphorus is melted it is pressed through the leather, keeping it always under the water; it is thus obtained pure, while there remains on the leather a quantity of red coloured matter, containing a little phosphorus. It has been affirmed by Steinacher, that the phosphorus purified in any of these ways still retains a little carbon, as, when kept in fusion, it deposites a little red matter, or if kindled, leaves a red trace. It is not very clear, however, that this red matter is, as has been affirmed, a carburet of phosphorus, and if it be, the quantity is very inconsiderable.

For convenience in keeping, and in making certain experiments with it, phosphorus is generally run into cylindrical pieces. This is done by having small funnels with cylindrical necks or tubes, the extremity of which is closed with a cork. They are placed in a perpendicular position under water, and some phosphorus cut into small pieces having been put into each, the water is heated sufficiently to melt the phosphorus; it sinks into the tube of the funnel, the water is allowed to cool, the phosphorus becomes concrete, and when perfectly cold is easily pushed out by the wide end of the tube. A method more expeditious, practised by Pelletier, was to fuse the phosphorus in a large quantity in water, to draw up a quantity of it in a glass tube by inspiring from it, to close the top of the tube by the finger, and remove it into a vessel of cold water; when the column of liquid phosphorus became immediately concrete.

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[*] Mémoires, tom. i. p. 253.

Phosphorus, when purified, is nearly colourless, or of a white colour, and semi-transparent. It has a consistence and tenacity similar to that of wax; it is rather harder, but can be easily cut by a knife. Its fracture often presents a radiated appearance. Its specific gravity is 1.714.

According to the observation of Pelletier, it is capable of crystallizing. When fused under water to prevent its combustion, on becoming again concrete, if the external crust be pierced and the liquid withdrawn, a crystallization in needles, like that of sulphur, or even in octohedrons if the cooling has been slow, is obtained. It also crystallizes by cold, from its solution in an essential oil *.

Its melting point is about 99 of Fahrenheit, though this varies as it is produced at different times, owing, as Pelletier supposes, to the presence of sulphur. At 219 it is volatilized, at 554 it boils in close vessels †.

When phosphorus is exposed to atmospheric air, it emits

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* Mémoires de Chimie de Pelletier, 1.256. † Ibid. p. 290.

fumes which have somewhat of a fœtid smell. When this experiment is performed in a dark place, the phosphorus is observed to be luminous, and it is in fact suffering a real combustion. This combustion is so slow, that it is not perceptible in day light, by any emission of light which accompanies it, and so little caloric is extricated that it can be easily held in the hand. At a higher temperature, as that of 100, the combustion is more vivid, and at 160 it burns with a bright flame, with the emission of a large quantity of caloric, and with the copious production of white vapours. The combustibility of phosphorus is much increased by its minute division, or by friction, so that, if rubbed moderately, the heat of the hand is sufficient to inflame it; and from this circumstance accidents have often happened in making experiments with it incautiously.

The combustion of phosphorus has been applied to the purpose of Eudiometry, and has been preferred by some chemists to any other method. It is performed either slowly, or is accelerated by the application of heat. In the latter mode, the result is sooner obtained, but it is inconvenient, as some contrivance is necessary to prevent part of the air from being forced out of the vessel, and as the combustion ceases before the whole of the oxygen is consumed, so that it is necessary to leave the phosphorus in contact with the air for some hours. The mode in which it is performed, is to fill a tube with mercury, and introduce into it a small bit of phosphorus, which rises to the top. It is then melted by approaching to the tube a hot iron. The air designed to be submitted to trial previously measured, is then slowly admitted, and the diminution of volume it has sustained is ascertained by again measuring it when cold.

The slow combustion of phosphorus is preferable as an Eudiometer. It can be performed over water; it requires no trouble, and has the important advantage of indicating when the process is finished. While any oxygen remains in the air subjected to experiment, the phosphorus is surrounded with a white vapour, observable in day light; and, in a dark place, it appears luminous. When the oxygen is entirely abstracted, these appearances cease, and the air around the phosphorus is perfectly transparent.

Gren applied the phosphorus to this purpose, by placing a tube graduated into 100 parts, filled with the air designed to be submitted to trial, on the shelf of the pneumatic trough, surrounded with water, placing beneath the orifice of it a small bit of phosphorus fixed on a cork to which a thread was attached. In this situation, the phosphorus absorbed the oxygen of the included air, and the cork rose on the water within the tube. When the process appeared to be finished, it could be withdrawn by the thread. This method, however, is extremely slow, and on this account the method of Berthollet, in which a larger surface of phosphorus is presented to the air, is to be preferred. A tube divided into 100 parts is filled with the air designed to be tried, and this air is transferred into another tube, somewhat larger, previously filled with water; a cylindrical piece of phosphorus is fixed on a glass rod, which is introduced into the vessel containing the air, so as to be exposed to it. The oxygen is gradually abstracted by the phosphorus. When the abstraction is complete, which is known by the disappearance of any whitish vapours, or any luminous appearance, the remaining air is transferred into the tube in which it was first measured, and the diminution of volume it has suffered is thus ascertained. The experiment is generally finished in from 2 to 6 or 8 hours, according to the size of the tubes in which the air has been measured, and exposed to the action of the phosphorus; the smaller the diameter of the tube in which the phosphorus is exposed, and the less the quantity of air, the effect being sooner produced.

There is one correction however to be made, to render the result accurate. It had been observed, that the diminution of volume which atmospheric air sustains from exposure to phosphorus, is less than that from other eudiometrical methods; and this has been found owing to a little of the phosphorus being dissolved in the residual nitrogen gas, and adding to its volume. This augmentation of volume, Berthollet states to amount to about a fortieth of the nitrogen gas. The observed diminution of volume produced by the phosphorus in atmospheric air, is about 20 in 100; leaving, of course, 80 of nitrogen. But, according to the preceding correction, a fortieth of this (or 2 parts) is to be added, to make the real diminution, and this gives 22 in 100. The method is sufficiently simple and easy, though certainly not superior to the solution of the alkaline sulphurets.

The phenomena exhibited by the combustion of phosphorus in oxygen gas at an elevated temperature, are such as might be expected compared with those which it presents in atmospheric air. The illumination is so vivid, that the eye can scarcely bear it, and there is the evolution of much heat. The nature of the product is the same.

But there is a singular fact for which chemists found it difficult to account,—that although in atmospheric air, phosphorus suffers a slow combustion at low temperatures, as at 50 or even 40 of Fahrenheit, it does not do so in pure oxygen gas, but requires to be heated to above 80, to exhibit even a faint combustion, and to 104 to burn vividly. We should expect that the spontaneous combustion would be more vivid in oxygen gas than in atmospheric air; but the reverse is the case; when a piece of phosphorus is placed in perfectly pure oxygen, no luminous appearance can be discovered even in the dark, at a temperature at which it would be luminous in atmospheric air, and it does not suffer any evident change.

This fact seems first to have been attended to by Göettling, a German chemist. He had observed, that phosphorus appeared luminous in nitrogen gas, even more than in atmospheric air; that it is thus changed into an acid, while in oxygen gas the appearance of combustion is more faint, and at length ceases. From these observations he drew conclusions unfavourable to the antiphlogistic theory. The subject soon engaged the attention of a number of chemists, and the facts with regard to it were ascertained. It has been shewn, that the luminous appearance of phosphorus in nitrogen gas is faint, and continues only for a short time; that if, after it has ceased, a little oxygen be admitted, the whole gas becomes immediately luminous. In a certain time this ceases, from the consumption of the oxygen; but if a fresh quantity be admitted, the luminous appearance is again produced. If the nitrogen be perfectly free from oxygen, such as that obtained from animal matter by dilute nitric acid, the phosphorus exhibits in it no luminous appearance even in the dark; but if a little of it is added to oxygen gas, a corruscation of light, of a blue shade, immediately occurs. The conclusions follow, therefore, that in pure nitrogen, phosphorus does not burn, but that the presence of oxygen is indispensable to its combustion and acidification.

The phenomena appear to depend on the solubility of phosphorus in nitrogen gas. It is proved particularly by the experiments of Vauquelin, that it is dissolved in small quantity by this gas, and that, when presented in this state to oxygen, the phosphorus and oxygen combine; hence the spontaneous combustion in atmospheric air. But, without this previous solution, a higher temperature is necessary, and hence the reason why phosphorus requires to be heated, to burn in oxygen gas. The luminous appearance which it exhibits in nitrogen gas, is owing to that gas not being pure, but containing a little oxygen, to which the dissolved phosphorus is presented, and its shining in oxygen gas is owing to a similar impurity from the admixture of nitrogen. From the experiments of Vauquelin and Brugnatelli it appears that hydrogen acts on phosphorus in a similar manner with nitrogen. A piece of phosphorus immersed in pure hydrogen, did not produce any light, but when, after a few hours, the gas which had been thus exposed was transmitted into a jar of oxygen gas, a vivid light was perceived. Nay, what is singular, it is proved that phosphorus is soluble in oxygen gas, without the phenomena of combustion being presented during the solution, while the luminous appearance is at once produced by the addition of nitrogen or hydrogen. This Vauquelin and Fourcroy established, by exposing phosphorus to pure oxygen gas for some hours; it had not in that time emitted any light, but on introducing to it nitrogen gas, a blue lambent light was immediately perceived. They endeavour to account for it, but perhaps not very satisfactorily, by the hypothesis, that in the simple solution of phosphorus by oxygen gas, there is no intimate combination, no decomposition of the gas and separation of its light and caloric; and that when nitrogen or hydrogen gas is added to the solution, it produces a separation of the particles of the phosphorus, a diminution, therefore, of their cohesion, and hence has the same effect as a slight elevation of temperature, which it is known is capable of causing phosphorus to burn in oxygen. Whatever, however, may be the probability of the theory as to this fact, the peculiar phenomena noticed by Göettling are sufficiently explained *.

Fourcroy and Vauquelin found, in their investigation of the preceding facts, that phosphorus does not become luminous in carbonic, sulphurous, muriatic, or fluoric acid, gas, or in ammonia; nor did any of these gases, after they had been exposed to it, produce any luminous appearance on the addition of oxygen. In nitric oxide gas, if introduced in a state of combustion, it continues to burn, and with nearly as much splendour as in oxygen gas. In oxymuriatic acid it melts, and, when the temperature is above 70 or 80 of Fahrenheit, burns with brilliant sparks, and with the production of copious white fumes. It exhibits a similar appearance in nitrous acid vapour. If a few

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* Annales de Chimie, t. xxi. p. 189. Ibid. t. xxii. p. 216. Nicholson's Journal, 4to, vol. i. p. 444. and ii. p. 8.

small pieces of phosphorus be put into nitrous acid, the acid soon begins to suffer decomposition by the phosphorus attracting oxygen, and very dense red coloured vapours are disengaged. If, by the violence of the effervescence, any of the pieces of phosphorus are buoyed up into this vapour, a flash of light is perceptible.

Phosphorus, in combining with oxygen, unites with it in different proportions, forming different compounds. When fully saturated, the result is an acid, inodorous and fixed, capable of being obtained in a concrete state; with a less proportion of oxygen, an acid is formed, having a slightly fœtid smell, somewhat volatile, and when heated exhaling a vapour which appears luminous in the dark. The former is named the Phosphoric, the latter the Phosphorous Acid. Besides these, the existence of an Oxide of phosphorus has frequently been supposed. The reddish matter with which the phosphorus is usually covered, or which it leaves as a residuum, when the combustion of it has been incomplete, or has been suddenly checked, and which is highly inflammable, has been considered as an oxide; but this has not been proved by any conclusive experiment, and its greater inflammability may be ascribed, perhaps, to its dryness. Some chemists have supposed, that it contains carbon derived from the impurity of the phosphorus. More, lately, Steinacher has affirmed, that the white vapour, which is sublimed when phosphorus is heated in a long and slender glass tube, and which condenses into a flocculent matter not acid, but capable of attracting humidity, and passing by exposure to the air into phosphorous acid, is an oxide at the minimum of oxidation, and that another white oxide at a maximum, is that which forms on the surface of phosphorus, which is kept long immersed in water, and which is also obtained by the action of liquid oxymuriatic acid *. The existence of these oxides is, however, problematical, and the two acids are the only well-determined compounds of phosphorus with oxygen.

Phosphorus enters into combination with hydrogen and with sulphur, forming compounds which are to be immediately described. It has been supposed too, particularly by Proust, to form a chemical combination with charcoal. This takes place in its distillation from charcoal and phosphoric acid, and constitutes the red matter, which, being less fusible than phosphorus, remains, when the phosphorus is melted, under water, and strained through leather. If it be distilled, he states, it yields what phosphorus was present, in excess; but the real combination is not subverted unless the degree of heat be much raised. But when it reaches ignition, a fresh quantity of phosphorus is sublimed, and the residue is charcoal. It burns easily when heated, but by exposure to the air becomes less inflammable †. It would require farther investigation to determine precisely the nature of this substance.

Phosphorus unites with many of the metals, forming compounds to be afterwards described. It enters into union with the metallic bases of the alkalis. Potassium being brought into contact with phosphorus in the air, there is a considerable action between them; they become fluid, and burn. Under naphtha they unite and form a com-

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* Nicholson's Journal, 8vo, vol. vi. p. 133.

† Ibid. 4to, vol. iv. p. 355.

pound which has a higher point of fusion than its two constituents, and which remains a soft solid in boiling naphtha. It has the appearance of a metallic phosphuret, is of the colour of lead, and has a lustre resembling that of this metal. Exposed to the air it is slowly converted into phosphate of potassa. With sodium results perfectly similar are obtained.

With the alkalis and alkaline earths, phosphorus enters into combination, when their mutual action is favoured by a high temperature, as by passing phosphorus in vapour over the ignited alkali or earth. These compounds are of a dark colour. Their chemical relations can scarcely be examined, as they rapidly decompose water, and are at the same time decomposed, phosphuretted hydrogen being formed.

Phosphorus is soluble in a number of inflammable liquids, such as oils expressed or volatile, alkohol, or ether, and forms fluids, which, by agitation with atmospheric air, or decomposition by water, produce illumination. The solution in expressed oil is prepared by putting two or three small pieces of phosphorus into a flask, pouring upon them a quantity of olive oil, and applying heat by a sand bath, until the phosphorus is dissolved. On rubbing the hand with this oil, it appears highly luminous in the dark, without being accompanied with any sensible emission of heat. A clear phial of moderate size, half filled with this oil, on being uncorked so as to admit fresh atmospheric air, affords as much light as in a dark place will render visible the figures on the dial of a watch. The solution of phosphorus can also be effected in the essential oils, as those of lavender or turpentine, though, from their volatility, more care is requisite in applying heat. These solutions are less luminous when agitated with the air.

Mr Accum has observed, that the phosphuret of sulphur is also soluble in oils, and that this forms a liquid much more luminous when exposed to the air than the solution of phosphorus alone. It dissolves by mere rubbing with the oil, and no heat ought to be applied, as it gives rise to an explosion. It is also soluble in essential oils, and these liquids are likewise luminous.

Alkohol, or ardent spirit, is likewise capable of dissolving phosphorus, a little of it being put with the alkohol into a strong phial well corked, and heat moderately applied. Very little is dissolved, but the alkohol acquires a perceptible odour, and if a little of this phosphuretted alkohol be dropt on water, a flash of light is disengaged from the surface of the water, which appears vivid in a dark place; or a feather dipt into water and immersed in the solution produces a similar luminous appearance. Sulphuric ether likewise dissolves phosphorus; but the solution does not give light when mixed with water. Both solutions are decomposed by water, and a turbid appearance is produced from the precipitation of phosphorus.

Phosphorus had been supposed in the arrangements of modern chemistry to be a simple substance. It has been stated, however, that Mr Davy has found, that when acted on by galvanism, it gives out phosphuretted hydrogen, and that he has concluded it is a compound of a peculiar base, with small quantities of oxygen and hydrogen.

SECT. II.

OF PHOSPHORIC ACID.

Phosphoric Acid is formed in the rapid combustion of phosphorus at a high temperature, either in atmospheric air or in oxygen gas. When the experiment is performed over mercury, it is obtained in the form of a white flocculent matter which is deliquescent, and hence becomes liquid on exposure to the air. Lavoisier, by many experiments, found that phosphorus, in burning, absorbs, as nearly as can be determined, 1½ part of oxygen, forming 2½ parts of acid, or, as he has stated it more minutely, 45 parts of phosphorus combine with 69.375 of oxygen, forming 114.375 of acid; 100 parts of phosphorus combine, therefore, with 154 of oxygen, which gives the proportions in 100 parts of acid, in the nearest round numbers, of 60 of oxygen and 40 of phosphorus.

Though its formation, by the immediate combination of its constituent parts, serves to demonstrate its composition and the proportion of its elements, the process is not the best that can be followed for procuring the acid, as it is tumultuous, and not easily managed so as to collect the product, at least unless a small quantity only of phosphorus is operated on. Other methods have therefore been followed.

It was imagined that the acid might be economically obtained by extracting it from bones. When bones are burnt to whiteness, they consist principally of phosphate of lime; and when this is acted on by sulphuric acid, it is decomposed. The decomposition however in this case is not complete, and the acid liquor obtained by washing the materials is not a pure phosphoric acid but a super-phosphate of lime. A marked difference was accordingly always observed between them. The pure phosphoric acid, when fused, forms a species of glass, but in this state it is still easily soluble in water, and is even deliquescent, while the glass that is obtained by evaporating the acid obtained from the action of sulphuric acid on burnt bones, and fusing it, is not deliquescent, and is very sparingly soluble in water, a difference owing to the presence of the portion of lime.

If we attempt, therefore, to prepare phosphoric acid in this way, some method must be followed to abstract the lime. Several have been proposed, but perhaps none can be perfectly relied on. By adding ammonia a considerable quantity of the lime is thrown down ; and by adding to the liquor after this a little carbonate of ammonia, a new precipitation is occasioned, from the joint affinities of the ammonia and the carbonic acid. I have already taken notice of this process as employed by Dr Higgins in the preparation of phosphorus ; and more lately it has been recommended by Bonvoisin to obtain pure phosphoric acid—carbonate of ammonia being added to the super-phosphate of lime to the point of neutralization, the phosphate of ammonia which remains in solution, being obtained by evaporation and crystallization ; and then being exposed to such a heat in a silver bason, as may be sufficient to expel the ammonia. Berthollet observes, however, that the phosphate of ammonia retains a portion of lime, which is rendered evident, by adding to its solution carbonate of soda; and although the acid obtained by evaporation and fusion is deliquescent and soluble, it is not perfectly pure. Gay Lussac has proposed to abstract the lime, by adding to the phosphoric acid concentrated by evaporation, oxalic acid, which unites with the lime, forming an insoluble precipitate; alkohol is added, which dissolves the pure phosphoric acid, and by evaporation this may be procured. The process is expensive, and Berthollet maintains that a little lime still remains with the acid, in conformity to the law that in such cases there is always only a participation of a base between two acids acting upon it *.

It is therefore necessary, in order to be certain of having the acid pure, to obtain it by the direct oxygenizement of phosphorus. It is not easy to do so by combustion, except on a very small quantity. The method Pelletier employed was to transmit a current of air through phosphorus in fusion under water kept near to a boiling heat †. Lavoisier employed nitric acid, throwing into it, heated a little on a sand bath, small pieces of phosphorus, successively as long as any decomposition of the acid took place, raising the heat towards the end of the process to assist the mutual action. The phosphorus received oxygen from this decomposition, and, by urging it with a strong heat at the end of the process, any undecomposed nitric acid was expelled ‡. The process given by Fourcroy appears more economical than any other. It consists in adding

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* Chemical Statics, p. 429.

† Mémoires de Chimie, t. i. p. 256.

‡ Journal de Physique, 1785, p. 1.

to the phosphorous acid, obtained by slow combustion in the manner already described, one-eighth of its weight of nitric acid of the specific gravity 1.3, and applying a gentle heat; the excess of phosphorus in the phosphorous acid receives oxygen from the nitric acid, and the product is pure phosphoric acid. It ought to be evaporated and fused in a silver or platina cup, as it acts not only on earthen vessels, but likewise on glass.

Phosphoric acid, as produced by the combustion of phosphorus, is in the form of a white spongy substance, which soon attracts humidity so as to become liquid. It then forms a dense oily-like fluid, colourless and inodorous. If exposed to heat, the water is evaporated, and at a temperature not greater than that of ignition it is fused, forming, when cold, a transparent glass. This, as has already been remarked, is deliquescent, and abundantly soluble in water, uniting with it in every proportion. It does not appear that it is volatilized by heat; and this great fixity, added to its affinity, renders it capable of decomposing, in the dry way, the compounds of many other acids.

Phosphoric acid has in a high degree the generic properties of acids. Its solution, even when much diluted, has a very sour taste, and immediately reddens the vegetable colours. It also exerts strong affinities to the alkalis and earths, and is superior, in the power of neutralizing their properties, to the other acids, with the exception of the Fluoric. It does not, however, exert much action on the metals, or on inflammable substances, apparently from the strong affinity with which its base retains the oxygen, and from the great condensation of the oxygen in the combination. Sulphur produces no change on it, even with the assistance of heat. Charcoal decomposes it at a high temperature, as has already been stated in considering the process for obtaining phosphorus. If heated in its concrete state with those metals which have a strong attraction to oxygen, one portion of the metal attracts its oxygen, and another portion combines with the phosphorus, and produces a phosphuret. It may be combined by the exertion of complex affinity with the metallic oxides, forming metallic salts, which are afterwards to be considered.

Phosphoric acid combines with the alkalis, forming salts denominated Phosphates. The alkaline phosphates are soluble and crystallizable; they are also fusible, forming a kind of glass, and facilitate much the fusion of a number of other substances. The acid is retained by so strong an affinity, by the fixed alkalis, that it is not decomposed when they are heated with charcoal. They are decomposed, at least partially, in the humid way, by sulphuric and some of the other acids; while, in the dry way, and at a high temperature, these decompositions do not happen; the phosphoric acid, on the contrary, from its fixity, being able to dislodge the more volatile acids.

PHOSPHATE OF POTASSA.—This salt, the result of the union of the phosphoric acid with potassa, has been little examined. It can scarcely be crystallized, as, by evaporation of its solution, a gelatinous mass is obtained; in this state, it attracts humidity from the atmosphere; its taste is saline with a degree of sweetishness. Exposed to heat, it becomes liquid, and, after the expulsion of the water, is fused by the application of a red heat into a glass, which is still deliquescent. It is decomposed both by lime and barytes. It has been applied to no use.

PHOSPHATE OF SODA.—This salt is better known, as its use is established, both in medicine, and for some chemical purposes. It is prepared, by adding to the acidulous phosphate of lime, obtained from the decomposition of burnt bones by sulphuric acid, as much of a solution of carbonate of soda as may be sufficient to saturate the phosphoric acid. The lime, in combination with a portion of phosphoric acid, is precipitated, and the water holding dissolved the phosphate of soda, is separated by filtration; by due evaporation the salt is crystallized. The crystallization is difficult and indeterminate if there be any excess of acid, while with a slight excess of alkali it is easily effected, and the crystals are large and regular; hence it is in general, as met with in the shops, slightly alkaline, so as to change to a green the syrup of violet. The form of the crystals is that of a rhomboidal prism, variously modified. They effloresce on exposure to the air, are soluble in 3 parts of cold water, and in half that quantity of boiling water. By heat, they are melted into a white opaque glass, which is readily soluble again in water. It is decomposed by barytes and lime, and by a double elective attraction by the magnesian and calcareous salts, and by many of the metallic solutions.

The taste of this salt is purely saline, without any bitterness. On this account it has been introduced into the practice of medicine as a substitute for the other aperient salts. As it melts easily, and promotes greatly the fusion of the earths and metallic oxides, it is used as a flux, in analyses performed by the blow-pipe.

PHOSPHATE OF AMMONIA exists in the urine of carnivorous animals, in considerable quantity, united with phosphate of soda, forming a triple salt, known to the older chemists by the name of Microcosmic, or fusible salt of urine. To obtain it pure, it must be formed by the direct combination of its principles. It is soluble in 4 parts of water at the temperature of 60; it crystallizes readily; the form of its crystals being a four-sided prism, acuminated with 4 planes; the crystals are neither efflorescent nor deliquescent. By exposure to heat, it is first fused into a transparent glass, and then decomposed, part of its ammonia being expelled. When mixed with charcoal, and exposed to heat, its acid is likewise decomposed, which is not the case with the other phosphates; hence it is solely from its decomposition that phosphorus is obtained from urine. It is likewise decomposed by the other two alkalis, by barytes, lime, and even by magnesia, so that the attraction between its principles is apparently not strong. Like the phosphate of soda, it may be used with advantage in analyses by the blow-pipe.

PHOSPHATE OF SODA AND AMMONIA, the triple salt above mentioned, as existing in several of the animal fluids, formerly engaged much the attention of chemists. From the researches of Fourcroy, it appears to be variable in the proportion of its elements, the quantity of ammonia, or phosphate of ammonia, diminishing as it is repeatedly crystallized. One variety obtained by a first solution and crystallization, he found to consist of 32 parts of acid, 24 of soda, 19 of ammonia, and 25 of water. It has generally an excess of alkali, effloresces in the air, is abundantly soluble in water, and very fusible, being at the same time partially decomposed when fused. It is an object of interest only as being found in the animal fluids.

PHOSPHATE OF BARYTES is easily formed, by decomposing phosphate of soda by muriate or nitrate of barytes. It is in the form of an insipid white powder, of considerable specific gravity: it is perfectly insoluble in water; is fusible at a high temperature; and is not decomposed by exposure to heat mixed with carbonaceous matter.

PHOSPHATE OF STRONTITES.—Phosphoric acid acts weakly on the native carbonate: the phosphate remains dissolved, while there is an excess of acid; but as this is neutralized, it is deposited in the state of a white powder, and if perfectly neutral, is very sparingly soluble in water, requiring about 2000 parts for its solution. It melts into an enamel by the flame of the blow-pipe; giving also a phosphorescent light. According to Vauquelin, it contains 58.76 of strontites, 41.24 of phosphoric acid.

PHOSPHATE OF LIME.—This compound exists native under different forms. It is also found in the ashes of some vegetable substances, particularly the farinaceous seeds, and it is contained in a number of animal products; it is in particular the basis of bones, and forms the earthy residuum obtained by their calcination. In the latter substance it is not perfectly pure, being mixed with a portion of carbonate of lime, and perhaps small quantities of other substances. It is obtained pure by dissolving the calcined bone in muriatic acid, and precipitating by ammonia; or by decomposing muriate of lime by phosphate of soda.

It is in its neutral state nearly or entirely insoluble in water; it exists, therefore, when artificially prepared, in the form of a white powder, though in nature it is found crystallized. It is quite insipid. Exposed to a very intense heat it is semi-vitrified, but not decomposed; nor is it even decomposed when heated with carbonaceous matter; the strong affinity exerted by the lime preserving the constitution of the phosphoric acid, and effectually counteracting the affinity of the charcoal to the oxygen of the acid. The acids decompose it more or less completely, by sharing the lime with the phosphoric acid; and if the compound of the lime with the acid employed in the decomposition be sparingly soluble, so as to be withdrawn, a soluble acidulous phosphate of lime is procured. Thus, if sulphuric acid is digested on calcined bones in powder, it attracts a portion of the lime, forming a sulphate of lime, which is of very sparing solubility. By washing the matter with water, a very acid liquid is obtained, which was once supposed to be pure phosphoric acid, but which still retains a portion of lime in combination, forming a super-phosphate. This has been regarded as a distinct salt by Fourcroy and Vauquelin, who have examined its properties: it is very soluble in water: by evaporation of its solution, it crystallizes in silky fibres, or in brilliant scales or plates: it is liquefied by heat, and forms even a transparent glass if it has been brought into perfect fusion; the aggregation of which is such that its sour taste is much diminished, and it is permanent in the air, though slightly deliquescent in its crystallized state. When heated with carbonaceous matter, the excess of acid which it contains above that which enters into the composition of the neutral phosphate is decomposed; and it is by this decomposition that phosphorus is obtained, as has been already explained. There is no reason, however, to regard this salt as one of uniform composition; on the contrary, lime may combine with variable and indefinite proportions of acid in excess; and in the decomposition of the neutral phosphate by different acids, it is not improbable that different super-phosphates of lime are formed, according to the energy of action in the decomposing acid. The compound, obtained by the action of sulphuric acid on calcined bones, is stated by Fourcroy and Vauquelin to be composed of 45 of lime, with 54 of phosphoric acid: the proportions of the neutral phosphate are, according to their analysis of it, 59 of lime, and 41 of acid *. Neither of these salts is applied to any use, except that from the super-phosphate, phosphorus is usually procured; and the calcined bone ashes made into a paste with water, are used in the fabrication of assaying tests and cupels.

PHOSPHATE OF MAGNESIA.—This compound is formed by the immediate solution of the earth in the acid; or it may be obtained more distinctly crystallized, by a process given by Fourcroy:—mixing equal parts of the solutions of sulphate of magnesia and of phosphate of soda; in a few hours pretty large crystals of phosphate of magnesia form. The crystals of this salt are compressed prisms: they effloresce speedily on exposure to the air; require at least 50 parts of cold water for their solution, but dissolve more abundantly in boiling water, so that the solution affords crystals on cooling. It is deprived of its water of crystallization when exposed to heat, and by a stronger heat is melted into a glass.

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* Mémoires de l'Institut National, tom. ii. p. 274.

Phosphate of Argil.—When phosphoric acid is combined with argil to saturation, it forms, according to Fourcroy, a white insipid powder. It melts before the flame of the blowpipe into a transparent globule.

Phosphate of Zircon is insoluble.

Phosphate of Glucine, obtained by decomposing nitrate of glucine by phosphate of soda, is in the form of a white powder, or of a viscous substance, insipid, and insoluble in water, but rendered soluble by an excess of acid. It is melted by heat, without decomposition, into a transparent vitreous globule.

Phosphate of Ittria, formed by complex affinity, on mixing a solution of phosphate of soda with the solution of a soluble salt of ittria, is insoluble, being thrown down in a gelatinous precipitate.

The combinations of phosphoric acid with the metals are to be afterwards described.

SECT. III.

OF PHOSPHOROUS ACID.

This acid is formed in the slow combustion of phosphorus in atmospheric air. It constitutes the white vapour which arises from the surface of the phosphorus, and which attracts water from the atmosphere, so as to be condensed and become liquid. Pelletier gave the following, as the easiest method of preparing it. A cylindrical piece of phosphorus of some length being put into a glass tube somewhat wide, a number of such tubes are prepared and placed in the mouth of a large funnel, the neck of which is inserted in a wide mouthed bottle placed on a flat plate containing a little water. Over this is placed a large bell jar to prevent the loss of the vapour, but having two apertures at the sides to admit of the circulation of air. The phosphorus slowly absorbs the oxygen of the air; by the pieces being placed in separate tubes, the risk of the whole taking fire from the heat produced even by the slow combustion is prevented; and the air within the jar being always kept humid by the water beneath, the acid vapours which are formed are condensed, and drop through the neck of the funnel into the bottle beneath *. By a process of this kind, Sage found, that three ounces of an acid liquor were obtained from one ounce of phosphorus.

The acid prepared according to the preceding method, has a considerable degree of specific gravity. Its smell is slightly fœtid, its taste extremely sour. It is abundantly soluble in water, and even when diluted instantly reddens the vegetable colours. When exposed to heat, part of the water is at first volatilized; but as this proceeds, a vapour is formed, which, disengaged at the surface, affords a dense white smoke, attended even with a luminous appearance, visible in the dark. By continuing the heat until this ceases, the phosphorous acid is deprived of its peculiar smell, and is converted into phosphoric. From this experiment, some chemists have been disposed to consider phosphorous acid as being rather phosphoric acid, holding

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* Mémoires de Chimie de Pelletier, tom. ii. p. 134.

a portion of phosphorus dissolved, than an immediate compound of phosphorus and oxygen in determinate proportions; the luminous vapour disengaged from it by heat being probably this phosphorus held in solution by the watery vapour, by the portion of air which the liquid might, from its formation by exposure to the atmosphere, have held dissolved, or by hydrogen derived from the decomposition by the phosphorus, aided by the temperature of a small portion of the water.

Phosphorous acid, by longer exposure to the air, passes very slowly, and even passes imperfectly, to the state of phosphoric acid,—a fact which, were the preceding theory just, would be a proof of the strong attraction exerted by the acid to the portion of phosphorus it is supposed to hold dissolved. By adding to it nitrous acid, it is at once converted to the phosphoric; if the nitric acid be diluted with water, it requires, to produce this effect, the assistance of heat. The oxymuriatic acid produces in the phosphorous acid the same change. The proportions of its constituent principles have not been ascertained, and from the successive transitions of which it appears susceptible, either when heated, or when exposed to the atmospheric air, there seems to be reason to believe that these proportions are not determinate, but that, by progressive oxygenizement, it may pass into phosphoric acid.

Phosphorous acid unites readily with the alkalis and earths, forming salts named Phosphites. These salts have scarcely been examined, but by Fourcroy and Vauquelin *. Vauquelin observes, that in several of their properties, they

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* Journal de l'Ecole Polytechnique, Cah. iv. p. 655.

resemble the phosphates. The alkaline phosphites, like the alkaline phosphates, are very soluble in water, and crystallizable, while the earthy phosphites are very insoluble, but become soluble by an excess of acid. The phosphites, however, may be at once distinguished from the phosphates, by appearing luminous when heated by the blowpipe, and by affording, by distillation, a small quantity of phosphorus. They detonate, too, with oxymuriate of potassa, and precipitate gold from its solution, in a metallic state. They pass very slowly into phosphates from exposure to the air.

Phosphite of Potassa.—Its solution yields, by evaporation, crystals, which appear to be four-sided prisms bevelled; its taste is somewhat sharp; it is very soluble in water. Heated by the blow-pipe, it swells up, and is melted, with the appearance of a phosphorescent light. It is decomposed by lime and barytes, and by the sulphuric, nitric, and muriatic acids. Fourcroy and Vauquelin found it to consist of 49.424 of potassa, 39.466 of acid, and 11.11 of water.

Phosphite of Soda is likewise very soluble in water, requiring at a mean temperature only about twice its weight; its solution, by slow evaporation, affords on the edge of the vessel feather-like crystals, and in the liquor itself, crystals in the form of plates. Exposed to the action of the blow-pipe, it decrepitates, and gives a phosphorescent light; it is then melted into a glass, which appears opaque on cooling. It consists of 23.68 of soda, 16.32 of acid, and 60 of water.

Phosphite of Ammonia is distinguished by a strong penetrating taste. Its solution affords delicate acicular crystals. Exposed to the blow-pipe, it swells up and is decomposed, a great quantity of phosphuretted hydrogen gas being disengaged, which burns vividly in the air, with the white circular smoke peculiar to the combustion of that substance. It is likewise decomposed by distillation in a retort, the ammonia being expelled partly in a liquid state, and partly in that of gas, and holding a small portion of phosphorus in solution, phosphoric acid being the residuum. It is decomposed by the other alkalis, by lime and barytes. According to Vauquelin, it consists of 51 of ammonia, 26 of acid, and 23 of water.

PHOSPHITE OF BARYTES is formed like the other insoluble barytic salts, by adding phosphorous acid, or an alkaline phosphite, to a solution of barytes, or of the muriate or nitrate of this earth. It is in the form of a white powder, insipid, and very sparingly soluble in water. It melts before the blow-pipe into an opaque globule, and is luminous during its fusion. Vauquelin states its composition at 51.3 of barytes, 41.7 of acid, and 7 of water.

PHOSPHITE OF LIME is formed by causing phosphorous acid to act on lime, until they are reciprocally saturated. The salt is insipid and insoluble; it is not altered by exposure to the air; heated it is phosphorescent, and urged by a strong heat it melts. It consists of 51 of lime, 34 of acid, and 15 of water. With an excess of acid it becomes soluble, and can be obtained in small prisms.

PHOSPHITE OF MAGNESIA is produced on adding the solution of an alkaline phosphite to a solution of sulphate of magnesia, appearing gradually in the form of a white flocculent precipitate. It is insipid, and so sparingly soluble, as to require 400 parts of water for its solution. Its solution suffers an imperfect crystallization. The salt, when heated, is phosphorescent, and melts. It consists of 20 of magnesia, 44 of acid, and 36 of water.

Phosphite of Argil is prepared by adding argillaceous earth to phosphorous acid. Its solution on evaporation becomes glutinous, but does not crystallize. It is soluble, and has a styptic taste. By heat it is not easily fused, but is rather decomposed.

SECT. IV.

OF PHOSPHURETTED HYDROGEN.

It has already been remarked, that phosphorus exposed to hydrogen gas is dissolved in small quantity, so that when this phosphuretted hydrogen is mingled with oxygen gas, a luminous appearance is produced; but besides this, a larger portion of phosphorus can be united with hydrogen, forming a compound possessed of peculiar properties.

This compound was discovered by Gengembre. Having shewn the nature of sulphuretted hydrogen, and observing the analogy between sulphur and phosphorus, he supposed that by subjecting phosphorus to a similar process, as that by which sulphur affords sulphuretted hydrogen, he might obtain a phosphuretted hydrogen. Having boiled, therefore, an alkaline solution with phosphorus, an elastic fluid was disengaged, of an offensive odour, and which had the singular property of catching fire when it came in contact with the atmospheric air [*]. Mr Kirwan, about the same time, led by the same analogical reasoning, had, without any knowledge of the experiments of Gengembre, made the same discovery. He obtained it by the same process, boiling an alkaline solution on phosphorus [†].

This is the process which is still followed for the production of this compound. On phosphorus, cut into small pieces, a strong solution of potassa is poured, in a retort the extremity of which terminates under water in the pneumatic trough; heat is applied by a taper, and the elastic fluid is disengaged, which takes fire when it escapes into the air. There is some difficulty in conducting the process, as the gas disengaged is apt to explode in the retort, when it mingles with the atmospheric air in the upper part of it; and if, to obviate this, the retort is filled nearly with fluid, this, on the application of the heat, comes over, and the gas is not properly produced. The best mode of obviating these inconveniences, is to fill the vessel with hydrogen gas, previous to the introduction of the phosphorus and alkaline solution, and, to prevent any risk, to use a brass bottle instead of a glass retort.

The theory of this process will be perceived, from what has been already stated under the history of sulphuretted hydrogen. The alkali, by combining with the phosphorus, and by the disposing affinity it exerts, enables it to decompose a portion of the water; one portion of it attracts oxygen, forming phosphoric acid; the hydrogen evolved combines with another portion of the phosphorus, and this compound assuming the elastic form is disengaged. Quicklime diffused in water, and boiled with phosphorus, likewise produces this gas. A solution of soda has the same effect as potassa, but ammonia, from its volatility, exerts little action on the phosphorus, and acquires only a slight smell *. Barytes and strontites act nearly as lime.

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[*] Journal de Physique, 1785, p. 276.

[†] Philosophical Transactions, vol. lxxvi. p. 150.

Dr Pearson discovered another method of producing phosphuretted hydrogen. In his experiments on the decomposition of carbonic acid by phosphorus, with the view of proving that the charcoal which is obtained from heating phosphorus with carbonate of lime is derived not from the lime or the phosphorus, but from the carbonic acid, he exposed to heat in a similar way, phosphorus with pure lime. Without obtaining charcoal, he thus formed a compound partly of a gray, partly of a reddish brown colour; on tasting it, he was surprised to find it explode on his tongue, and on throwing it into water, bubbles of an elastic fluid were disengaged, which exploded on coming into contact with the air †. The process for preparing this phosphuret of lime is to coat a glass tube 8 or 9 inches long, and ½ inch wide, with clay and sand; to put into the bottom of it about a drachm of phosphorus in small pieces and dry; over this are put small pieces of well-prepared quick-lime, so as to fill the tube, putting at the top a little pounded lime, to exclude the air more effectually, and closing the tube with a small plug of clay. It is then placed across a choffer or small portable furnace, so that the middle of the tube is raised to a red heat; the

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* Journal de Physique, tom. xxvii. p. 280.

† Philosophical Transactions, 1792, p. 303.

phosphorus at the end of the tube is thus sufficiently heated to be volatilized, and passing over the red hot lime, it enters into combination with it, a small portion generally escaping at the same time from the mouth of the tube, and taking fire. The phosphuret of lime is of an auburn colour; it is kept in bottles well stopt, to exclude the access of humidity. When a piece of it is thrown into water, bubbles of phosphuretted hydrogen gas are rapidly produced, which flash as they rise from the surface of the fluid, the lime in this preparation enabling the phosphorus to decompose the water, as the alkali does in the other Dr Pearson found, that by a process similar to the preceding, a dry phosphuret of potassa could be prepared, which thrown into hot water produced a similar inflammable gas; and a similar combination of phosphorus with barytes and strontites exerting the same agency may be formed.

There is reason to conclude that phosphuretted hydrogen is variable in its proportions. The gas which is first disengaged, when an alkaline solution is boiled on phosphorus, though it produces a white cloud when it comes in contact with the atmospheric air, does not burn; but it appears to become more inflammable as the process proceeds, probably from the proportion of phosphorus being augmented. And when even the highly inflammable gas is kept for a day or two over water, it loses its inflammability. It is not improbable, therefore, that there is a gradation in the proportion of phosphorus from that which hydrogen gas takes up when phosphorus is exposed to its action in the cold, to that which is evolved highly inflammable in the preceding processes.

It is possible, too, that oxygen may enter into the composition of this gas, as it does into that of what is named Sulphuretted Hydrogen. It has not been observed, however, to have any acidity.

Phosphuretted hydrogen is permanently elastic; it is absorbed in small quantity by water, 100 cubic inches absorbing, according to Henry, 2.14 cubic inches of gas, but, according to Raymond, distilled water dissolves about one-fourth of its bulk by agitation. The smell of the gas is unpleasant, similar to that which attends putrefaction; that of the watery solution, though different, is likewise disagreeable, as is also its taste; its colour is a pale yellow. The gas is again expelled from it by heat, unchanged; it has no effect on the vegetable colours; by exposure to the air it is decomposed.

But the most characteristic property of phosphuretted hydrogen gas, is its high inflammability, which it derives no doubt from the phosphorus it contains being in the most favourable state for combining with oxygen, deprived of cohesion, and not retained by any strong affinity. The moment it comes in contact with atmospheric air, it inflames with a vivid flash of light and a slight explosion; nor can they be presented to each other with safety, but in small quantities. If bubbles of the phosphuretted hydrogen gas be received successively in oxygen gas, the combustion is still more vivid, and the explosion, at the breaking of each bubble, such as to convey a sensible impression to the hand placed on the jar. It likewise inflames, when received in oxymuriatic acid gas; nitric oxide gas produces, when mixed with it; a white vapour, and diminishes its inflammability [*]; but if oxygen be added immediately, the heat produced from its combination with the nitric oxide appears sufficient to cause the inflammation, even of the less inflammable gas. An accident, producing severe injury, happened to Pelletier from making a mixture of this kind of these three gases [†].

A singular and beautiful appearance presents itself in the inflammation of this gas in atmospheric air. When the bubble of gas breaks, there is a flash of light, and this is accompanied with a dense white vapour, which rises in the atmosphere, extending itself circularly, so as to form a horizontal ring; this ascends in a calm atmosphere to the height of several feet, enlarging as it rises, so that before it breaks it is often more than a foot in diameter. This white cloud consists of watery vapour wafting phosphorous acid, the one being produced by the union of the oxygen of the atmosphere with the hydrogen of the gas, the other by its union with the phosphorus; but it is somewhat difficult to account for this regular appearance being assumed. Probably, as Dr Higgins has expressed it, "the "flocculent phosphoric acid, and aqueous vapour, may be "thrown by the eccentric impulse of the explosion into "the form above described, and buoyed in the air until "the ring is cooled or dissipated [‡]." A similar appearance, no doubt arising from a similar cause, is often to be observed in the discharge of artillery.

In receiving this gas in a jar over mercury, and afterwards transmitting into it successive small portions either of atmospheric air or oxygen gas, though the vivid inflammation is at first produced, Gengembre observed, that the gas at length no longer inflames, though it is still capable of burning brilliantly when kindled in contact with atmospheric air; a proof that the phosphorus of the phosphuretted hydrogen is more disposed to burn at a low temperature than the entire compound, and that, in the combustion, a portion of the hydrogen, retaining probably a little phosphorus, does not burn *.

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[*] Philosophical Transactions, vol. lxxvi. p. 152.

[†] Mémoires de Chimie, t. i. p. 313.

[‡] Minutes of a Society for Philosophical Exper. p. 278.

Its watery solution decomposes a number of the metallic solutions, and throws down dark coloured precipitates, which appear to be metallic phosphurets. Its relations, especially in its elastic form, to other chemical agents, have not been minutely examined, from the difficulty of subjecting it to experiment.

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Trommsdorff having observed a gas to be produced in the decomposition of phosphoric acid by charcoal at a high temperature, which when freed from the carbonic acid mixed with it, and burnt, afforded water, carbonic acid, and phosphoric acid, concluded it to be a ternary compound of carbon, phosphorus and hydrogen. He describes it as being of nearly the same specific gravity as atmospheric air, insoluble in water, not affected by oxygen at common temperatures, but exploding with it when heated †. It is not improbable, however, that it may be a mixture of a little phosphuretted hydrogen with carbonic oxide, and a variety of oxycarburetted hydrogen.

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* Journal de Physique, tom. xxvii. p. 278.

† Nicholson's Journal, 8vo, vol. iii. p. 302.

SECT. IV.

OF PHOSPHURETTED SULPHUR.

Sulphur and phosphorus are capable of being chemically combined, the combination taking place apparently in indeterminate proportions, forming what may be named a phosphuret of sulphur, or a sulphuret of phosphorus, according to the excess of either ingredient. The combination was first observed by Margraaf, and afterwards examined more particularly by Pelletier *.

It may be effected by the immediate application of heat to the phosphorus and sulphur, but this method is attended with some risk. If the two substances be put into a retort connected with a receiver in which is some water, on applying heat, the combination Pelletier remarked takes place with such rapidity and violence, that a portion of the mixture is thrown from the retort with an explosion, and the vessel is frequently broken. The method he employed was to put the two substances in a matrass with a quantity of water, and apply heat sufficient to melt the phosphorus; its combination with the sulphur then takes place with less violence; though even in this way Pelletier remarked that sometimes part of the compound was thrown from the matrass, particularly when the proportions used were about equal parts of sulphur and phosphorus, and when the heat was a little too quickly applied †.

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* Memoires de Chimie, tom. i. p. 281.

† Mémoires de Chimie, tom. i. p. 293.

This compound is more fusible than the phosphorus itself. The fusibility appears to be greatest when they are combined in equal proportions, the compound melting, or rather, when liquid, congealing at a temperature of 41° ; with one of sulphur to two of phosphorus, the compound congeals at 50° ; and with one to 4 at 60° ; when, on the other hand, the sulphur is in larger proportion, it becomes less fusible ; the compound of one of phosphorus with two of sulphur congeals partially at 56°, and that of one of phosphorus with three of sulphur at 99°.

Pelletier observed that this combination has a tendency to decompose water. Though he took every precaution of employing distilled water, of washing with care the phosphorus and sulphur, and of applying the heat, so that no part of the phosphorus should be made to burn ; yet still in a few days the water was strongly acid ; and the decomposition was besides indicated by a fœtid odour, in which that of sulphuretted hydrogen, and of phosphuretted hydrogen could be distinguished, and by the disengagement of a vapour which appeared luminous in the dark. Hence, as Pelletier remarked, the water probably suffered decomposition by its oxygen being attracted by the phosphorus and sulphur, forming the acids which result from their oxygenizement, while the hydrogen was disengaged holding portions of these substances dissolved, and giving rise to the peculiar odour and the luminous appearance*.

This decomposition of water, and production of a gas easily inflamed, appears to be well established from an accident related by Mr Accum, as arising from an experiment, in which half an ounce of phosphorus cut in small pieces had been introduced into a Florence flask, containing about ten ounces of water, and one ounce of sulphur added. Heat having been applied, and continued for about ten minutes after the union of the sulphur and phosphorus had been effected, the flask became filled with dense white fumes, and, on removing it, and agitating the fluid, the whole exploded with much violence. The experiment on half the quantity of materials was repeatedly made with a similar result. And by applying the heat gradually to a mixture of phosphorus and sulphur, with water, in a Wedgwood's tube terminating by a bent tube in the mercurial trough, a large quantity of gas was collected, which inflamed when mixed with atmospheric air, producing sulphur, sulphuric acid, and phosphoric acid *.

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* Mémoires de Chimie, t. i. p. 294.

Dr Briggs has confirmed these facts by some additional observations. The decomposition of the water commences when the union of the sulphur and phosphorus takes place; and if the temperature is raised to 210, is very rapid, the gas disengaged being highly luminous in the dark, and holding sometimes dissolved so much phosphorus as to take fire on coming into contact with the air, and form the ring of white vapour, which the combustion of the pure phosphuretted hydrogen displays †.

He has supposed, that the compound formed under water is not a pure phosphuret of sulphur, or sulphuret of phosphorus; but that these bases are in the state of oxides, having received oxygen from the water; whence their greater inflammability. He has also given a process

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* Nicholson's Journal, vol. vi. p. 1. † Ibid. vol. vii. p. 58.

by which the sulphur and phosphorus may be combined with safety in the dry way, forming a product somewhat different. It consists in filling a glass tube, hermetically sealed at one end, with sulphur and phosphorus, corking it firmly, and plunging the tube into warm water, the heat of which is to be gradually raised until it boil. The sulphur and phosphorus unite without violence; and, after removing the tube from the water, it is to be shaken that the mixture may be complete. The young chemist will of course be cautious, however, in attempting to perform an experiment of this kind.

This compound, when a small proportion of sulphur has been used, is solid when cold, has a crystallized appearance, and a yellowish white colour, while that formed under water is described as having a friable texture, spongy appearance, and a sulphur yellow colour. The former, though more inflammable than phosphorus, is not so much so as the latter; but it may be rendered equally inflammable, by setting fire to it while it is still in the tube in which it was prepared, by plunging a hot wire into it, and allowing it to burn for 5 or 6 seconds. It is thus, as Dr Briggs has supposed, converted into an oxide of sulphur and phosphorus, and is so inflammable, that the instant a little of it is brought into the air, it catches fire. From the great inflammability of these compounds, they are used for procuring easily a lighted match, and form the best kind of phosphoric match-bottles. The proportion used for this purpose, is said by Mr Accum to be one part of sulphur with eight of phosphorus; but much less of sulphur, as a thirtieth, is preferable, as the combination is equally inflammable, and is less soft.

CHAP. V.

OF MURIATIC ACID AND ITS BASE.

THREE Acids, Muriatic, Fluoric, and Boracic, had been known to chemists for a considerable period, but had resisted all the means of analysis applied to them. It was therefore only from analogy that they were regarded as compounds, and as containing oxygen as a constituent principle. By the application of galvanism to these acids, however, this has been more directly established; phenomena have been produced, to be stated under the history of each, indicating their decomposition, though their bases have not yet been obtained in an insulated state.

Muriatic Acid, besides the state in which it exists in many natural combinations, and from which it can be obtained unaltered, is capable of combining with oxygen in two proportions, so as to form other two acids, very different in their properties. The present chapter will include the history of these three acids, and of their saline combinations.

SECT. I.

OF MURIATIC ACID.

This acid exists in large quantity in a combined state in the mineral kingdom. The combination of it with soda forms the neutral salt, which is the principal ingredient in the water of the ocean, and which is also deposited in immense beds in the earth, forming what has been named Rock Salt. The acid exists in sea water in other combinations, particularly with magnesia; and with soda, magnesia, and lime, in many mineral springs. It serves to mineralize some of the metals, and it is found in a number of the products of the vegetable and animal system.

To discover the composition of this acid has always been an object of much interest to chemists; and within these few years the inquiry has given rise to several suppositions, which were always however very imperfectly supported, and of which perhaps it is scarcely necessary to take notice, as the perfect analysis of the acid will probably soon be effected. Girtanner had supposed that hydrogen is its base, as, when it was subjected to the action of oxidifiable substances, hydrogen gas was evolved. But it was obvious that this might be derived from the water of the acid; and that this is its origin was proved by the experiments of Van Mons * and of Tassaert †, and still more decidedly by Mr Henry, who, in submitting muria-

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* Mémoires de l'Institut National, t. i. p. 36. 44.

† Annales de Chimie, tom. xxix. p. 308.

tic acid gas to the action of electricity, found hydrogen to be produced in a very limited quantity, and obviously in relation to the portion of water which the gas held dissolved *. More lately Berthollet, supposing that this acid is produced in different cases of chemical action, where water and nitric acid are formed or decomposed, inferred that its base is a compound of hydrogen and nitrogen, or that it is a ternary compound of these gases and oxygen †; but the facts in support of this conclusion were never established with sufficient precision. The apparent production of muriatic acid in the decomposition of water by galvanism, gave rise likewise to different speculations with regard to its composition, which fell to the ground when the fact was established by the experiments already stated (p. 134), that water, if perfectly pure, affords no trace of this acid, when it has been submitted to galvanic action.

Mr Davy, in his late investigations, has submitted muriatic acid to experiment, with a view to effect its analysis. On heating potassium in muriatic acid gas, as dry as it could be obtained by common chemical means, there was a violent chemical action with ignition; and when the potassium was in sufficient quantity, the muriatic acid gas wholly disappeared, and from one-third to one-fourth of its volume of hydrogen gas was evolved, and muriate of potash was formed." This hydrogen had probably been produced from the water combined with the acid. Admitting this, Mr Davy remarks, from the quantity produced, " that muriatic acid gas must contain at least one-eighth,

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* Philosophical Transactions, 1800.

† Nicholson's Journal, 4to, vol. iv. p. 378.

or one-tenth of its weight of water; and that the water oxygenates in the experiment a quantity of potassium, sufficient to absorb the whole of the acid." The quantity of water thus indicated in muriatic acid gas, it is added, is much greater than the quantity indicated by the action of electricity in Dr Henry's elaborate experiments.

Some results on this subject still more singular have been more recently stated. Mr Davy has inferred from his experiments that muriatic acid gas contains at least one-third of its weight of water, and the presence of this water appears to have a very surprising effect with regard to its acid powers. The acid itself could not be procured free from water in an uncombined state. But combinations of it were procured with phosphorous acid, phosphoric acid, sulphuric acid, and with phosphorus; and these compounds, though composed of matter intensely acid, do not act on litmus paper nor dissolve alkalis, and they are also non-conductors of electricity. But a very small quantity of water developes their energies, renders them conductors, and enables them to act powerfully on vegetable colours and on alkaline bodies. With these compounds of muriatic acid, potassium detonates violently, even at common temperatures probably decomposing the muriatic acid.

From the prosecution of these interesting experiments, the constitution of this acid will probably soon be discovered.

Muriatic acid is always procured from sea salt, which is a compound of it with soda. Two parts of the salt, which has been previously exposed to a red heat, to consume any extractive matter adhering to it, are put into a retort, and one part of sulphuric acid is poured upon it. An effervescence at first takes place, from the disengagement of muriatic acid gas, but this soon ceases. The retort having been previously placed in a sand bath, and being connected with the bottles of Woulfe's apparatus containing water, heat is applied; the muriatic acid gas continues to be disengaged, a portion of which is condensed in the first bottle by the water which distils over from the materials, but the greater part passes in the gaseous state into the portions of water in the other bottles by which it is absorbed. The application of the heat is continued as long as there is any disengagement of gas. To avoid the effervescence that attends the pouring the sulphuric acid on the dried muriate of soda, some chemists dilute it previously with half its weight of water; and in this case, more of the product is condensed in the first bottle. One part of acid to two of muriate of soda, though the proportion generally given is perhaps scarcely sufficient. Vauquelin recommends 3 parts to 4. Beaumé has affirmed, that after the production of muriatic acid gas has ceased, a new quantity may be obtained by unluting the vessels, introducing a portion of hot water to the materials, and applying heat; a practice which from what we know of the effect of water in promoting the expulsion of gaseous bodies from fixed combinations, may perhaps be advantageous. The chemist generally performs this process in glass vessels; but when prepared for purposes in the arts, it is sometimes done in an iron pot to which an earthen head is adapted. The residuum of the process is sulphate of soda, with an excess of acid, the sulphuric acid remaining in combination with the soda, while the muriatic acid from its weaker affinity or greater volatility has been disengaged.

Even when the distillation has been carried on in glass vessels, the product, at first obtained, is never perfectly pure. It is more or less of a yellow colour, while the pure muriatic acid gas combined with water is colourless. It is not very certain to what this colour is owing. Some have supposed it to arise from a small quantity of sulphur remaining in the sulphuric acid, and brought over by the muriatic acid gas; and likewise to the presence of a little oxymuriatic acid; others have ascribed it to the extractive matter which adheres to the muriate of soda obtained by evaporation from sea water; and that this is in part just, appears to be proved by the fact, that the yellow colour is greater when the salt has been used without having been exposed to a red heat, than when this preliminary operation has been performed. It seems principally, however, to arise from the presence of iron contained in the sea salt, derived from the iron vessel in which the evaporation of sea water is performed. It is obtained pure by subjecting it to a second distillation from a retort connected with a range of Woulfe's bottles, a little muriate of soda having been put with it into the retort, and a moderate heat being applied. The muriatic acid gas is disengaged and absorbed by the water in the bottles, forming a solution that is free from colour.

This is not to be regarded as the real acid, but only as a combination of it with water, to which it owes its liquid form. The muriatic acid uncombined, exists always in a gaseous state. This gas may be obtained, simply by applying to the liquid muriatic acid a moderate heat. It is disengaged, and as it is absorbed by water with the greatest rapidity, it must be received over quicksilver, when it remains permanently elastic. It can equally be procured by adding to muriate of soda, half its weight of sulphuric acid, and, after the first effervescence is over, applying a very gentle heat, the extremity of the retort being placed under a jar inverted in the pneumatic trough filled with quicksilver; a very large quantity of gas is disengaged. This is the process generally employed to obtain it for experimental purposes.

Muriatic acid gas has a peculiar pungent smell; when inspired, even diluted with atmospheric air, it occasions a sense of suffocation; and in its concentrated state, if received alone into the lungs, is fatal to life. When confined over mercury, and dry, it is colourless, and therefore invisible; but when presented to atmospheric air, white vapours are formed which arise from its combination with the aqueous vapour present; hence they are more copious in a humid atmosphere. Its specific gravity, according to Kirwan, is to that of atmospheric air as 1929 to 1000.

Muriatic gas is not inflammable; and it is incapable of supporting combustion. A lighted taper immersed in it, is extinguished, the flame previously assuming a green tinge.

When exposed to the action of the electric spark, its volume is enlarged. This, Mr Henry has shewn, arises from the decomposition of the portion of water which it holds dissolved. It ceases after a certain time, but on admitting a drop or two of water is renewed.

The attraction of muriatic acid gas to water is strong; it combines with it with great rapidity, and is condensed in very large quantity, the water taking up not less than 360 times its volume of the gas. Its bulk is by this absorption increased about one-third, and its weight doubled. The absorption is attended with the production of heat. Ice exposed to this gas is instantly melted, and the temperature falls,—a curious fact, as proving that the liquefaction of a solid absorbs more caloric, than the condensation of a gas into the liquid state gives out.

A fact somewhat singular appeared to be established by Mr Kirwan's experiments with regard to the combination of muriatic acid with water, in different proportions. The other acids, the sulphuric for example, or the nitric, when mixed with water in various proportions, suffer condensation from the combination, so that the specific gravity of the mixed fluid is not the mean specific gravity of the acid and water; and as it differs in different proportions, requires to be discovered by experiment. But mixtures of liquid muriatic acid, with additional proportions of water, appear not to suffer condensation, and hence the specific gravities may be found by calculation, as they correspond with the mean specific gravities of the acid and water. This peculiarity, as Berthollet remarks, "probably depends on the muriatic acid gas, in its passage "to the liquid state, experiencing so much condensation "from the great quantity of water that is required, that "an increase in the proportion cannot exercise a force on "it which will produce a sensible alteration in the state "in which it is found."

In its gaseous state, 100 cubic inches of muriatic acid weigh, according to Mr Kirwan's estimate, 60 grains: 10 grains of water absorb 10 grains of the gas under a medium atmospheric pressure, and at the temperature of 49; the liquid acid occupies the space of 13.3 grains nearly; hence its specific gravity is 1.500. The specific gravity of the strongest acid that can easily be procured is 1.196. By calculation, 100 parts of this will be found to contain 49 of that, the specific gravity of which is 1500; and as the quantity of real acid which this contains is known from the above experiment, the quantity in the other is also discovered. By mixing this acid of the specific gravity of 1.196 with different proportions of water, Mr Kirwan formed the following table of the quantities of real muriatic acid in liquid acids of different specific gravities*:

In *Muriatic Acid* of different Densities, at the Temperature of 60°.

100 Parts Spec. Grav.	Real Acid	100 Parts Spec. Grav.	Real Acid.
1,196	25,28	1,1282	16,51
1,191	24,76	1,1244	15,99
1,187	24,25	1,1206	15,48
1,183	23,73	1,1168	14,96
1,179	23,22	1,1120	14,44
1,175	22,70	1,1078	13,93
1,171	22,18	1,1036	13,41
1,167	21,67	1,0984	12,90
1,163	21,15	1,0942	12,38
1,159	20,64	1,0910	11,86
1,155	20,12	1,0868	11,35
1,151	19,60	1,0826	10,83
1,147	19,09	1,0784	10,32
1,1414	18,57	1,0742	9,80
1,1396	18,06	1,0630	8,25
1,1358	17,54	1,0345	5,16
1,1320	17,02	1,0169	2,58.

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* Transact. of the Irish Academy, vol. iv. p. 4. and vol. vii. p. 163.

The muriatic acid of commerce, which is often known by the old name of Spirit of Salt, is never saturated with the gas. Its specific gravity seldom exceeds 1170. In this state, however, it is strongly acid. A single drop of it is sufficient to redden the more delicate vegetable colours; it is corrosive, and when largely diluted, still tastes extremely sour. It exhales white vapours, of a pungent, suffocating odour, when presented to the atmospheric air, an appearance owing to part of the muriatic acid gas escaping from the liquid, and combining with the aqueous vapour of the atmosphere. This shews that it is not retained by water by a very strong force; and this also is proved by another fact, that on adding to the liquid muriatic acid a little concentrated sulphuric, an effervescence is produced from the expulsion of the muriatic acid gas.

As it is incapable of directly affording oxygen, it does not act with much energy on the metals; charcoal, sulphur, and phosphorus, are scarcely affected by it. By a disposing affinity, however, it enables a number of the metals to decompose the water present and receive the oxygen; it thus dissolves them, those, especially, which exert a strong attraction to oxygen, as iron or zinc, the solution being attended with the extrication of hydrogen gas. It also exerts a strong affinity to the metallic oxides, and decomposes many of their combinations with the other acids. Its most delicate test, and that which discovers it in all its combinations, is derived from the affinity it exerts to oxide of silver, and from forming with it a dense precipitate, so that a few drops of nitrate of silver added to any liquid containing the smallest proportion of muriatic acid, gives rise to a cloudiness from the production of this insoluble compound.

This acid combines with the alkalis and earths, forming salts named Muriates. Their taste is that termed peculiarly saline; they are soluble and crystallizable, are not decomposed by heat, at least this is the case with the alkaline muriates; they are partially decomposed by the sulphuric acid, and if heat be applied to favour the elasticity of the muriatic acid, the decomposition is nearly complete.

MURIATE OF POTASSA.—This salt is contained in vegetables, and makes part of the saline matter extracted from their ashes after combustion. It may be prepared either by the immediate combination of its constituent parts, or by the decomposition of muriate of soda, by the potash of commerce, a process sometimes followed to procure soda. Its taste is saline and bitter; it requires three parts of cold water for its solution; boiling water dissolves half its weight of it, the solution crystallizing on cooling, though not with regularity. The form of its crystals obtained by spontaneous evaporation is a cube. They are slightly deliquescent. Exposed suddenly to heat, they decrepitate; by an increase of heat the salt is fused and volatilized, without decomposition. They consist, according to Bergman, of 61 parts of alkali, 31 of acid, and 8 of water. According to Kirwan, when dried at the temperature of 80, the salt consists of 64 of alkali and 36 of acid.

Muriate of potassa is decomposed by the sulphuric and nitric acids, which combine with its base. By the sulphuric acid, the muriatic acid is disengaged on the application of heat, and is obtained pure; but in the decomposition by the nitric acid, as this acid is disposed to assume the gaseous form, the muriatic acid disengaged is always mixed with it, and part of it at the same time receives from the nitric acid an excess of oxygen, forming a compound acid named nitro-muriatic. In the dry way the phosphoric acid also dislodges the muriatic. By barytes a partial decomposition is occasioned, the acid being divided between the two bases. Clay and siliceous earth effect a partial decomposition in it, by the attraction they have to its alkali.

Muriate of potash is not much used; it has sometimes been employed as a flux in melting some of the metals, to protect them from the action of the air; and it is employed in the manufacture of alum to afford its alkali.

Muriate of Soda.—This salt is one of the most abundant productions of nature, and exists native in much greater quantity than any other neutral salt. The waters of the ocean owe their saltness to it; it is found in a number of mineral springs, and it forms immense strata in the earth, or rising on the surface, even to the height of mountains. According as it is produced from these sources it is named Sea salt, or Rock salt.

Rock salt is in general a very pure muriate of soda, and when freed from its earthy intermixture, and the small quantity of colouring matter, by solution and evaporation, affords the salt in its purest state. The salt contained in saline springs is also in general purer than that from the water of the ocean, though not always so. The proportion of muriate of soda contained in sea water, varies considerably in different latitudes according to the degree of evaporation. The quantity of saline matter on an average amounts to about $\frac{1}{25}$; and of this rather more than $\frac{3}{4}$ths are muriate of soda.

The salt is procured by processes which are varied according to situation. In very cold climates, the water being received into shallow ditches during the winter, is frozen, by which a great part of the superfluous water is removed, and the remaining liquor affords salt by artificial evaporation.

In warm climates it is obtained by spontaneous evaporation. The water is received into broad shallow trenches at the sea-side, without the reach of the tide. The bottom of these is made of clay well beaten, and they are divided into several compartments. The fluid being thus spread out on an extensive surface, quickly evaporates, and by sluices it is removed from one space to another, so that when it arrives at the last, it is a strong brine, and the salt is soon deposited. It is necessarily mixed with the clay of the ground, and with several of the neutral salts and other impurities which sea water contains. Salt prepared in this manner is known by the name of Bay Salt.

In colder climates recourse must be had to artificial evaporation. The water is heated in shallow iron pans. Muriate of soda possesses the singular property that it is as soluble in hot as in cold water; after due evaporation, therefore, it begins to crystallize on the surface of the hot liquor; the crystals as they increase fall to the bottom of the vessel, are raked out, and set to drain. This is the process by which it is obtained in this country.

Sometimes this method is conjoined with natural evaporation. The sea-water, before it is received into the boiler, is pumped into a reservoir, under which faggots of thorns, &c. are suspended. It is allowed to drop over these, and a large surface being thus presented to the atmosphere, while the air is also rapidly renewed, much of the water is evaporated. It is then conveyed to the boiler, and evaporated in the usual manner. Or, in some of the northern departments of France, the sea-water is made to flow over a bottom of clay covered with sand, which favours both the evaporation of the water and the concretion of the salt; the saline deposite which is at length formed, is lixiviated with sea-water, which becoming thus more impregnated with salt, is concentrated by boiling so as to afford it by hasty crystallization.

Sea-salt obtained by any of these processes, is never perfectly pure. Seawater contains, besides muriate of soda, several other neutral salts, particularly muriate of magnesia, muriate of lime, and sulphate of soda. These being more soluble in hot than in cold water, remain dissolved in the hot liquor, from which the salt crystallizes. A small quantity of them, however, adheres to the muriate of soda. They render it deliquescent, give it a bitter taste, and considerably impair its antiseptic power. Different processes have therefore been contrived to obtain the salt free from these foreign salts. The most simple is to procure it by a slow artificial evaporation. It then crystallizes with scarcely any mixture of the others. This is the cause of the superior purity of the bay salt. Hence also the larger the crystals of sea-salt are, they may be justly supposed to be the purer, as the largeness of the crystals is owing to the slowness of the evaporation by which they are formed.

Another ingenious method was proposed, and put in practice by Lord Dundonald. The salt to be purified is put into a conical vessel, placed with the small end undermost, and having an aperture at the bottom. There is poured upon it a boiling hot solution of common salt. This dissolves any of the muriate of lime, or of magnesia, or indeed any other salt which may be mixed with the sea-salt; as the solution is saturated, none of the latter is dissolved; and by repeating the washing, it is obtained nearly pure. By three washings, it is rendered purer than salt prepared by any other process.

For chemical purposes, muriate of soda is most easily purified, by dissolving it in water, and adding to its solution a solution of carbonate of soda, till no cloudiness is produced by the addition. Every foreign salt is thus decomposed and precipitated, and the strained solution will contain the pure muriate of soda, which may be crystallized.

Muriate of soda has a salt, rather agreeable taste, being when pure free from all bitterness; it is soluble in rather less than 3 parts of water at the temperature of 60, according to Bergman in 2.8, according to Kirwan 2.5, and is scarcely more soluble in water at any higher temperature, even to 212°, requiring at this temperature, according to Bergman, 2.76. Hence its hot solution does not crystallize by cooling; the evaporation must either be carried on till the salt separates, in which case the crystallization is confused, or it must be left to spontaneous evaporation, when it concretes in crystals which are regular cubes, of a larger size and more regular form as the evaporation has been more slow. These crystals neither deliquesce, nor effloresce, on exposure to the air; the common sea-salt indeed is deliquescent; but this is owing to the muriates of magnesia and lime which adhere to it. Exposed to heat, the crystals of muriate of soda decrepitate from the sudden conversion of their water of crystallization into vapour. If the temperature is raised to a red heat, the salt melts; in an intense heat it is volatilized in white vapours, without undergoing decomposition.

Crystallized muriate of soda contains, dried at 80°, in the hundred parts, according to Mr Kirwan, 53 of soda, and 47 of acid, containing, however, some water of composition, so that of real acid the quantity is 38.83. Its specific gravity is 2.12.

This salt is decomposed by the sulphuric and nitric acids, in the same manner as the muriate of potassa is. It is from its decomposition by the sulphuric acid that the muriatic acid is best obtained, as has already been observed. When decomposed by nitric acid, part of the latter is decomposed, a quantity of its oxygen being transferred to the muriatic.

None of the other acids decompose it in the humid way, but the phosphoric and boracic are able to effect its decomposition when assisted by a high temperature, the muriatic acid being much more disposed than either of these acids to assume the gaseous form, and this tendency, joined to the attraction of either of these acids to the soda, effecting the decomposition.

One of the most important practical problems in chemistry is to decompose this salt, so as to obtain its alkali. It abounds so much in nature, that if such a process, capable of being carried on to advantage, could be discovered, a vast supply of soda would be obtained; and as this alkali can be employed for every purpose that potassa can, and is superior to it for some uses, such a discovery would be of much importance to the chemical arts.

Barytes might effect its decomposition, at least partially, and disengage a portion of the base; but the difficulty of obtaining this earth in an uncombined state, independent of any other objection, prevents such a process from being employed. Lime will produce likewise a partial decomposition, either when used pure, or combined with carbonic acid, but experiment proves it to be slow, and to be soon stopt, from the solubility of the muriate of lime which remains in the mass in a state capable of counteracting the formation of the carbonate of soda, or decomposing it if it were formed. By the soda receiving carbonic acid from the atmosphere, and efflorescing above the mass when pure lime is used, and by a similar efflorescence of it when carbonate of lime is employed, a certain quantity can indeed be procured; and in this way, Berthollet has shewn, as has already been stated (p. 90.), that the formation of carbonate of soda, in some natural situations, takes place. But the quantity of materials that would be requisite, and the length of time necessary to the decomposition being complete, prevent it from being applicable in practice.

Potassa in the state of the potash of commerce has been used as the medium of decomposition. There is here indeed the obvious objection, that we only substitute one alkali for another. Still, however, from local circumstances, this process may often be followed with advantage. Though the decomposition must be partial, it appears from the experiments of Westrumb, that the product of soda is considerable; 20 lbs. of sea-salt are dissolved in 60 lbs. of water, and 25 lbs. of the potash of commerce added, boiling the liquor until a saline pellicle forms on its surface, and begins to be deposited. On allowing it to cool, much muriate of potassa is deposited. When cooled to 50°, on removing it into another vessel carbonate of soda begins to crystallize, and from the above quantity of ingredients, 25 lbs. at an average are obtained, which however requires, by subsequent solution and crystallization, to be freed from a little muriate of soda adhering to it, by which it is reduced to 20 lbs *. As muriate of potassa answers as well as the carbonate in the manufacture of alum, or the preparation of nitre, where it can be applied to these uses, this process may be advantageously followed, as it may also where potassa is recovered in an impure state from certain processes in the arts in which it is employed, as, for example, in the ley remaining in the manufacture of soaps. This method has been employed with advantage in this country.

Another kind of decomposition of muriate of soda, which has sometimes been carried on, on a large scale, is, that by the medium of the oxides of lead. Scheele observed, that in mixing four parts of oxide of lead with one part of sea-salt, making the mixture into a paste with water, and allowing it to stand in a soft state for a little time, adding water occasionally to keep it in this state; the oxide of lead attracted the muriatic acid, and the soda might be extracted by washing the mass with water. This method has been carried into practice, the sea-salt and the

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* Annales de Chimie, tom. vi. p. 21. ; tom. xiii. p. 213.

oxide of lead being triturated together, and afterwards lixiviated, and the soda being combined with carbonic acid so as to be obtained under the form of the crystallized carbonate, either by leaving the solution exposed to the atmosphere, or by evaporating, and calcining the saline matter with charcoal or saw-dust, at a red heat, from which carbonic acid would be formed, and attracted. The drawback on the process, is the large quantity of oxide of lead which is required. The decomposition appears to be effected by the affinity of the oxide of lead to the muriatic acid aided by its quantity, promoted too by the insolubility of the muriate of lead, with excess of oxide. Hence three or four parts of oxide of lead are required to decompose fully one of muriate of soda. In the patent for this method which Mr Turner had in this country, the sub-muriate of lead was, by the application of heat, converted into a yellow pigment, by which the expence was defrayed *. But the demand for this was not sufficiently extensive to admit of the process being carried on on a large scale. The sub-muriate of lead may, by roasting, and calcination with charcoal, be reduced to the metallic state; but the expence of oxidating the lead, and then reducing it, is such as to render the method generally impracticable. In some cases only where lead contains silver, and is oxidated to obtain that metal, advantage is taken of this, and the two operations are combined.

The most practicable method, on the whole, and that from which the greater part of the carbonate of soda in the market is at present furnished, is that where the muriate

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* Repertory of Arts, vol. xii. p. 157.

of soda is decomposed by sulphuric acid, and the sulphate of soda afterwards decomposed by carbonaceous matter with various additions, such as lime, iron, &c. This gives rise to several varieties of the general process, an excellent summary of which, as well as of the other methods, was given in a report on this subject by Lelievre, Pelletier, Darcet, and Giroud *, and liberally published by the French government.

The muriate of soda is decomposed in the usual mode by sulphuric acid; and to defray the expence, the muriatic acid is collected and employed in the manufacture of sal-ammoniac, in the preparation of oxymuriatic acid for bleaching, or for any other useful purpose to which it can be applied. The sulphate of soda is calcined in a reverberatory furnace, to free it from any superfluous acid. It is then to be decomposed. Were the decomposition of it effected merely by exposing it to heat with charcoal powder, or any other convenient carbonaceous matter, though the oxygen of the sulphuric acid would be abstracted by the carbon, the sulphur would be attracted by the soda, and from this sulphuret of soda it would not be easy to obtain the pure alkali: Heat, it has been found, is not sufficient, as part of it only can be volatilized, while at the same time part is converted into sulphurous acid, which again combines with the alkali; hence the necessity of the various additions which are made, with the view of attracting the sulphur.

Lime may be employed for this purpose; and the first process described in the report above referred to, consists

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* Annales de Chimie, tom. xix.

in mixing sulphate of soda with an equal weight of chalk, which is a carbonate of lime, and rather more than half its weight of charcoal in powder, and exposing them to heat in a reverberatory furnace, sufficient to bring them into a state of imperfect liquefaction. An elastic fluid containing much sulphur is disengaged, and burns at the surface, the matter being frequently stirred to facilitate its expulsion. When this has ceased, and the matter, in cooling, is observed to have assumed a fine grain, the process is considered as finished; the mass is exposed to a humid atmosphere, and after some time carbonate of soda is extracted from it, 100 lbs. affording 37½ lbs. of the carbonate crystallized. The charcoal decomposes the sulphuric acid, the sulphur is in part expelled by the heat, and in part combined with the lime, while carbonic acid is afforded to the soda, and its combination with the sulphur thus counteracted. This, in the opinion of the authors of the preceding report, is the process which, where peculiar local circumstances do not favour any of the others, is the best.

Iron is also used. A process of this kind described in this report, consists in mixing sulphate of soda calcined, 200 lbs. charcoal, partly in powder and partly entire, 62 lbs. and pieces of white iron or iron plate, 65 lbs.; the mixture of salt and charcoal being exposed to heat, and the iron added in successive portions, is at length brought completely into fusion; after being cold it is lixiviated, and affords from 100 lbs. of salt, 71 lbs. of crystallized carbonate of soda, the residual matter being sulphuret of iron with a little charcoal. Malherbe and Athenas, who reduced this method to practice, proposed to use instead of iron some varieties of iron ore, of the hæmatitic kind, and also to decompose the muriate of soda by sulphate of iron instead of pure sulphuric acid.

Both iron and lime may be used with advantage at the same time: And the different processes above described have been combined in various modes, for which, in this country, patents have often been obtained *. The sulphate of soda which remains in the preparation of the oxymuriatic acid for bleaching, has within these few years been subjected to operations of a similar kind, and the process is carried on on a large scale with advantage.

Still, in any of these latter processes, the alkali obtained is not pure, but contains a little sulphur from which it is not easy to free it, which may be detrimental in some uses to which it is applied, and which, by gradually passing to the state of sulphurous acid by absorbing oxygen, will of course diminish the power of the alkali. Dizé, by whom the process by the medium of sulphate of soda, chalk, and charcoal, was carried on, has, in an investigation of this subject lately published, stated, that oxide of lead is capable, in the humid way, of abstracting the greater part or the whole of the sulphur. The ley obtained by washing the mass resulting from the decomposition of sulphate of soda by charcoal and carbonate of lime, is of a yellowish colour, and gives a precipitate of sulphur, attended with a disengagement of sulphurous acid and sulphuretted hydrogen, when an acid is added to it. But if a quantity of semi-vitreous oxide of lead, the litharge of commerce, in powder, be added to it while in ebullition,

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* Repertory of Arts, vol. iv. vii. ix. x.

the ley becomes colourless, and affords no sulphur, sulphurous acid, or sulphuretted hydrogen, but only carbonic acid, on the addition of an acid, and contains, therefore, the alkali pure. Oxide of manganese was substituted for oxide of lead with equal success; it is much cheaper than the other, and it has the advantage that it can be repeatedly used, merely by calcining it each time, so as to expel the sulphur *. By the same method, barytes may be freed from the sulphur combined with it when sulphate of barytes is decomposed by charcoal; and thus be applied to the decomposition of sulphate of soda.

Muriate of soda is of extensive use. Its application to preserve animal substances from putrefaction is well known; the theory of its antiseptic quality has never been properly explained. It is also taken universally as a seasoning to food, and seems to be necessary to promote digestion, as even the lower animals, it has been proved, languish when altogether deprived of it. It is employed in a variety of arts. In the manufacture of pottery of the coarser kind, when it is thrown into the oven in which the ware is baked, it is converted into vapour, and being applied in this state to the surface of the vessels, glazes them, an effect probably owing to the combination of its alkali with the siliceous earth of the pottery. It is employed in the manufacture of glass, which it is said to render whiter and clearer; in that of soap, which it makes harder; as a flux in the melting of metals from their ores; and in a variety of chemical and pharmaceutical processes.

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* Philosophical Magazine, vol. xxiii. p. 70.

Muriate of Ammonia.—This salt, the result of the combination of muriatic acid and ammonia, is the Sal-Ammoniac of commerce, and has been long known under this name. It is found as a product of volcanoes and pseudo-volcanoes; but in small quantity, and for use, is always prepared by art.

A manufacture of this kind had been established in Egypt from time immemorial. It is procured, according to the account that has been given, by sublimation from the soot of fuel *. Large quantities of it have been prepared in Europe for a number of years past, so that the Egyptian sal-ammoniac is no longer imported.

The process, which is kept in some measure secret, is different in different manufactories. The soot of coal by maceration in water affords a quantity of sulphate of ammonia. This having been obtained by crystallization, is mixed with muriate of soda; the mixture, after being well dried, is exposed to a strong heat. A double decomposition takes place; the sulphuric acid of the sulphate of ammonia unites with the soda of the muriate of soda, while the muriatic acid combines with the ammonia. The muriate of ammonia is sublimed to the top of the vessel, the sulphate of soda remains at the bottom. Sulphate of ammonia is also sometimes procured by obtaining an impure ammonia by distillation from animal substances, saturating it with sulphuric acid, obtaining the salt by evaporation, and exposing it to heat mixed with muriate of soda, in the manner above described. Another process said to be followed, is to disengage the muriatic acid from the muriate of soda by the sulphuric acid in the usual manner, to combine it with the impure ammonia, and afterwards sublimed the compound salt. In all these processes, a considerable part of the expence is defrayed by the sulphate of soda, which is at the same time procured.

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* Philosophical Transactions, vol. li. p. 504.

From the manner in which this salt is prepared, by sublimation in large glass globular vessels, it is always in the form of semi-spherical cakes, having a polished surface, and a texture somewhat ductile, of a greyish colour more or less white, often with a tinge of red, from the presence of a small quantity of muriate of iron. It is however capable of crystallization by solution in boiling water and cooling, its crystals being tetrahedral prisms acuminated by 4 planes. They suffer little or no alteration by exposure to the air, at least if they deliquesce it is in a very inconsiderable degree.

The taste of this salt is acrid and cool. It requires about 3½ times its weight of water, at the temperature of 60, to dissolve it, its solution being accompanied with a reduction of temperature. Boiling water dissolves nearly its own weight of it. Exposed to heat, it is volatilized, even before it is melted, and with little or no decomposition. Its specific gravity is 1.42. According to Kirwan, 100 parts of sublimed muriate of ammonia consist of 28 of ammonia, 42.75 of acid, and 29.25 of water.

Muriate of ammonia is decomposed by the sulphuric and nitric acids, which combine with its alkali, and by potassa, soda, barytes, and lime, which unite with its acid. It is by the latter of these decompositions that ammonia is usually obtained, as has been already stated. It is also decomposed by the carbonates of potassa, soda, and lime, by which the carbonate of ammonia is obtained.

Muriate of ammonia is used in many of the arts. In soldering, it cleans the surface of the metals to be united, and prevents their oxidation; in dyeing, it renders several colours brighter; and it is often used in pharmacy and in a number of chemical processes.

Muriate of Barytes is formed either by dissolving the native carbonate in diluted muriatic acid, or by adding to the sulphuretted hydro-sulphuret of barytes obtained from the decomposition of the native sulphate by charcoal, muriatic acid to the point of neutralization, filtering the solution, and evaporating it until on cooling it crystallize. The crystals of muriate of barytes are quadrangular tables, bevelled on the edges: they are soluble in 3 parts of cold water; and are more soluble in hot water, the solution affording crystals on cooling. It is also soluble in alkohol, and gives to the flame of the alkohol in burning a yellow tinge. From exposure to the air, it suffers no alteration. When heated, it decrepitates, and loses its water of crystallization, but is not decomposed. According to Kirwan, it consists, when crystallized, of barytes 64, acid 20, water 16; according to Vauquelin, of barytes 60, acid 24, water 16 *. It affords a re-agent extremely delicate, to discover the presence of sulphuric acid in any combination.

Muriate of Strontites is formed by the action of dilute muriatic acid on the native carbonate: when not diluted, the acid scarcely acts on it, unless heat be ap-

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* Journal de l'Ecole Polytech. Cah. III. p. 47.

plied. The solution, by evaporation and cooling, affords crystals, which are slender hexaedral prisms. These are deliquescent in a humid atmosphere: they are very soluble in water; one part of water, at 60°, dissolving one and a half, and, in boiling water, they appear to dissolve in any quantity, the water of crystallization itself being sufficient to keep the salt in solution. Exposed to heat, they lose 42 *per cent.* from the escape of the water: by a red heat, the salt is completely fused; but its acid is not expelled. The stronger heat, however, excited by the flame of the blowpipe, causes its decomposition. It consists, according to Vauquelin, of strontites 36.4, acid 23.6, water 40.

MURIATE OF LIME is sometimes contained in mineral springs, but is most easily obtained by the action of muriatic acid on carbonate of lime, the carbonic acid being disengaged, and the muriatic acid combined with the lime. Its taste is extremely bitter, and somewhat acrid: it is very soluble in water, the water dissolving even when cold more than its weight of the salt, and forming a liquid, which, from its concentration, is of a thick consistence. Its solubility is greater in hot water; and the solution, by cooling, affords crystals, which are regular if removed before the whole solution has by cooling and rest formed a crystalline mass: their form is a six-sided prism acuminated by six unequal planes. It is extremely deliquescent; the crystals being with difficulty dried, and very quickly attracting humidity from the air. And it is in consequence of this strong attraction to water, that this salt acts with so much energy on snow, liquefies with it, and, by this liquefaction, occasions intense cold. Exposed to heat, it suffers the watery fusion: when the water is dissipated, and the heat increased, a small portion of its acid is expelled. The residual matter is phosphorescent, and was formerly known by the name of Homberg's Phosphorus.

It is decomposed by several of the acids, as the sulphuric or phosphoric, which disengage the muriatic acid, and by the fixed alkalis, which precipitate the lime: it suffers decomposition too from several of the neutral salts: its solution, mixed with a concentrated solution of carbonate of potassa, forms a gelatinous or even solid substance, the water present being absorbed by the carbonate of lime. Crystallized muriate of lime consists, according to Bergman, of lime 44, acid 31, water 25: after exposure to a red heat, the proportions of its constituent parts are, according to Kirwan, 50 of lime, 42 of acid, and 8 of water.

Muriate of Magnesia.—This salt is that which, next to muriate of soda, is contained in largest quantity in sea-water. As it is very difficultly crystallizable, it remains after the sea-salt has been crystallized, and forms the principal constituent part of the bittern. It is likewise found in salt springs, and in mineral waters.

It has a very bitter nauseous taste; the nauseous taste of sea-water arising principally from it. It is very soluble in water, and can scarcely, indeed, be obtained in the solid form. By evaporating its solution to the consistence of jelly, and exposing it to a sudden cold, acicular crystals are formed: these deliquesce rapidly, on exposure to the air. It is likewise soluble in alkohol, and communicates to it the property of burning with a yellow or reddish flame. Exposed to a strong heat, it is decomposed, its acid being driven off. It consists, when dry, of 31.07 of magnesia, 34.59 of acid, and 34.34 of water.

Muriate of Argil.—Muriatic acid dissolves argillaceous earth with facility. The solution can scarcely be brought to crystallize, but forms, by evaporation, a gelatinous mass, which is deliquescent, and is decomposed by heat, its acid being expelled. It has the astringency of the other argillaceous salts.

Muriate of Glucine is very soluble in water; by evaporation it can be obtained in small crystals. Muriate of Zircon has an astringent taste, is very soluble in water, and in alkohol; by evaporation of its watery solution it forms transparent needle-like crystals, which are efflorescent. Muriate of Ittria is obtained by evaporation of its solution in a gelatinous form.

Muriatic acid appears to be capable of acting on siliceous earth. When the silex is in that state of division in which it is when precipitated from its alkaline solution, it is even sensibly dissolved by this acid, and, as has been already remarked, the solution by evaporation becomes gelatinous; by urging the mass with a stronger heat the acid is expelled.

The metallic muriates fall to be considered under the history of the metals.

SECT. II.

OF OXYMURIATIC ACID.

MURIATIC ACID enters into combination with oxygen, forming compounds, possessed of very peculiar properties. The different acidifiable bases are susceptible of different degrees of oxygenizement; but with regard to all of them, the acid powers are increased by an additional proportion of oxygen; and the most powerful acid formed from any base is that in which it is saturated with oxygen. To this general law, muriatic acid presents a striking exception. By combination with oxygen, its acid powers are diminished instead of being increased, so much so, that some chemists have supposed the compound ought not to rank as an acid. It has a styptic rather than a sour taste; instead of reddening, it destroys the vegetable colours, and its affinities to the alkalis or earths are less strong. It possesses, however, the most distinctive property of an acid, that of completely neutralizing the alkaline properties, and forming saline combinations, and hence may still be placed under this order.

In consequence of this singularity in the combinations of muriatic acid with oxygen, a peculiar nomenclature has been applied to denote them. Instead of employing, in conformity to the usual nomenclature, the terms Muriatous and Muriatic, the acid in its primary state retains its appellation of muriatic acid, as being the most powerful acid. The compound which is formed by its first combination with oxygen has been named Oxygenated Muriatic Acid, which Mr Kirwan afterwards contracted into Oxymuriatic Acid. Still another compound can be formed in which there is an additional proportion of oxygen, and which has been named Hyper-Oxygenated, or Hyper-Oxymuriatic Acid. The terms Oxymuriatic Acid, and Hyper-Oxymuriatic Acid, are, on the whole, the most convenient to express these combinations, and regarding the syllable *Oxy* not as the radical, but as an abbreviation of oxygen, may, as has been already remarked, be received as sufficiently correct.

Oxymuriatic Acid is a compound for the discovery of which we are indebted to Scheele. It cannot be formed by the direct combination of its constituent principles,—the muriatic acid and oxygen, in their gaseous form. But by presenting them in a nascent state, or even in certain combinations in which they are deprived of their elasticity, and not retained by a strong affinity, they unite; and it was by a process of this kind accidentally observed, that Scheele effected their combination, and discovered this form of the acid.

In investigating the nature of a mineral substance which had attracted his attention, that, since known by the name of black oxide of manganese, he observed, that in dissolving it in muriatic acid, a gas was disengaged, of a yellow colour, and of a peculiar suffocating odour, very similar to that of the vapour disengaged during the mutual action of nitric and muriatic acids; and in the farther investigation which this observation led to, he found, that by distilling the muriatic acid from the black oxide of manganese in a retort, into a receiver, an acid gas was obtained, having qualities altogether different from those of the muriatic. Several of these he pointed out, particularly its more sparing solubility in water, its inferior acid power, its peculiar energy in destroying the vegetable colours, and its power of dissolving with facility the greater number of the metals. In conformity to the theoretical opinions then received, he supposed that the muriatic acid was deprived of phlogiston by the black oxide of manganese that to this the change in its properties was owing; and hence he gave to this new product the name of Dephlogisticated Muriatic or Marine Acid *.

Berthollet prosecuted this investigation. In conformity to the theory of Lavoisier then advanced, he concluded, that the muriatic acid in its distillation from the black oxide of manganese receives oxygen, and that to this the new properties it acquires are to be ascribed. This he proved, by shewing that black oxide of manganese contains oxygen, and is capable of affording it; that when previously deprived of it, muriatic acid is no longer changed by it, and that from this peculiar product, which in conformity to this theory he named oxygenated muriatic acid, oxygen might be expelled by a very simple experiment, that of exposing it to the rays of the sun, when it returned to the state of simple muriatic acid †. He likewise observed several of its properties and chemical relations, and to him we are indebted for its application to the process of bleaching, an application of perhaps the great-

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* Chemical Essays, p. 90.

† Mémoires de l'Acad. des Sciences, 1785, p. 276.

est practical utility of any that has ever immediately resulted from the labours of a scientific chemist.

The process that was first employed to obtain this acid was that described by Scheele; diluting muriatic acid of the usual strength with an equal weight of water, and distilling it from one-fourth of its weight of black oxide of manganese. But the process succeeds equally well, and is more economical when the materials from which the muriatic acid is obtained are mixed with the oxide, and the mixture is exposed to heat.

Four parts of muriate of soda are mixed with rather more than one part of black oxide of manganese in powder; the mixture is put into a retort, and there are poured upon it three parts of sulphuric acid previously diluted with two parts of water. An effervescence takes place from the disengagement of the elastic fluid, and the upper part of the retort is tinged of a yellowish green colour. On applying heat, the oxymuriatic acid is more abundantly formed and disengaged. If the object of the experiment be to obtain the oxymuriatic acid in combination with water, the retort is placed in a water bath, and connected with the bottles of Woulfe's apparatus, in which the water is placed, and with which the acid, in being transmitted through it, combines; what condenses in the first bottle is not pure oxymuriatic acid, but consists partly of unchanged muriatic acid, holding dissolved even a little oxide of manganese; the gas without this impregnation passes into the other bottles, and absorbed by the water affords the liquid oxymuriatic acid pure. If the object be to obtain the acid in its elastic form, heat is applied by the medium of a lamp or taper, and the gas is received over water, the temperature of which is about 90°, as at this temperature the water absorbs scarcely any of it, and it is not only more convenient to operate with water than with quicksilver, but the latter is even less fit as being acted on by the oxymuriatic acid gas.

In this process the sulphuric acid combines with the soda of the muriate of soda, and disengages the muriatic acid, and this acid receives oxygen from the black oxide of manganese, and is thus converted into the oxymuriatic. At the end of the process, the black oxide of manganese is found deprived of much of its oxygen, or reduced from the *maximum* to nearly the *minimum* of oxidation. With this imperfect oxide of manganese, a portion of the muriatic acid combines, forming a muriate of manganese that remains mixed with the sulphate of soda; and to the affinity of the muriatic acid to this imperfect oxide, the formation of the oxymuriatic acid has been ascribed.

The composition of oxymuriatic acid is indicated, not only by its formation, but likewise by its decomposition. A very satisfactory experiment of this kind was long ago performed by Berthollet, from which he inferred the proportions of the oxygen and muriatic acid existing in it. When exposed to solar light, it is decomposed, its oxygen assuming the elastic form: 51.1 cubic inches of the liquid acid, by exposure to the rays of the sun for several days, gave 15.27 cubic inches of oxygen gas. The quantity of muriatic acid remaining in the liquid was discovered, by adding to it nitrate of silver; the muriate of silver formed amounted to 383 grains: this Berthollet concluded, from the usual estimate of the composition of this salt, contained 65 of muriatic acid; and hence it follows, that

100 of oxymuriatic acid consist of 89 of muriatic acid, and 11 of oxygen.

Mr Chenevix executed its analysis in a mode somewhat different. The compound formed by passing a current of oxymuriatic acid gas through a dilute solution of potassa was obtained by evaporation. It consists partly of muriate, and partly of hyper-oxymuriate of potassa. The latter salt gives no precipitate with nitrate of silver, the former does; 100 grains of the entire mass, obtained by evaporation, were therefore precipitated by nitrate of silver, when a quantity of muriate of silver was obtained, which, by proportions previously determined, Mr Chenevix knew corresponded to 84 of muriate of potassa; hence 16 parts of the 100 must have been hyper-oxymuriate of potassa. But, according to the proportions of this latter salt, ascertained from its decomposition by heat, as is to be afterwards stated, 16 of it contain 6 of oxygen, with 3.2 of acid: And, by other experiments, 84 of muriate of potassa were found to contain 27.88 of muriatic acid. Hence there existed in the entire salt, 27.88+3.2 of muriatic acid, or 31.08 parts, and 6 of oxygen, forming the oxymuriatic acid, from which that salt had been produced, which in 100 parts make the proportions of the constituent parts of that acid 84 of muriatic acid, and 16 of oxygen.

Berthollet has more lately supposed, that in this method there is a source of error, from part of the oxymuriatic acid being disengaged in the evaporation, and another portion of it decomposed: and in experiments which he has made, he obtained rather a less proportion of the hyper-oxymuriatic than that above stated. The error, however, cannot be great, and when the results of the method Berthollet himself employed are corrected by an alteration which Mr Chenevix found ought to be made in the estimate of the proportion of muriatic acid in muriate of silver, they agree very nearly with the other, 100 of the oxymuriatic acid with that alteration consisting of 85 of muriatic acid, and 15 of oxygen *; and Berthollet has since admitted these proportions.

Oxymuriatic acid, when uncombined, is elastic under a common atmospheric pressure, though by great pressure Mr Northmore succeeded in condensing it into a liquid †. It is heavier than atmospheric air; it has a yellowish green colour, and, from possessing colour, is the only permanently elastic fluid that is visible. Of all the gases it is the most insupportable to animals. When pure, it occasions immediate death, if an animal is immersed in it; and even when largely diluted with atmospheric air, it cannot be respired with safety; it occasions a severe sense of stricture at the breast, which renders it impossible to make a full inspiration; and this continues even for a considerable time after it has been inspired.

Oxymuriatic acid gas is absorbed by water, the quantity being larger as the temperature is low, but much less than the quantity of muriatic acid which water absorbs. At 50° the water does not appear to take up more than twice its volume. In this absorption a singular phenomenon occurs when the temperature is below 40°. As the water becomes saturated with the gas, small soft scales appear to form in the liquid, which increase as the absorp-

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* Chemical Statics, vol. ii. p. 169.

† Nicholson's Journal, vol. xiii. p. 134.

tion proceeds, inclosing the fluid part until the whole become of a gelatinous appearance, or even congealed; and, under favourable circumstances, regular crystals of the form of a quadrangular prism have been formed. This concrete matter melts on the application of a very moderate heat, and the gas even rises in bubbles through the liquid. It is the combination of the oxymuriatic acid with water. The gas itself, when obtained dry, is incondensible by cold; if transmitted through water, so as to be saturated with it, it is condensed by a low temperature; and the compound of it with water is so much disposed to congelation, as to suffer this at 40° of Fahrenheit: in this congelation, however, Berthollet supposes that the oxymuriatic acid does not retain much water combined with it. The fact is a singular one, and it is rendered still more so by another, that the oxymuriatic acid, in combining with water, does not part with much caloric, as the temperature is scarcely sensibly raised, nor is the liquid much heavier than water,—a proof that the gas has not experienced a great condensation from the combination.

The saturated solution of the oxymuriatic acid gas in water has a yellowish green colour; it has the intolerable odour of the gas itself; the taste is not sour, but harsh and styptic, and it possesses equally, as in the elastic form, the property of destroying the vegetable colours. The gas is expelled by raising the temperature. By exposing it to light, the acid is decomposed, as has been already remarked; oxygen gas is disengaged, and it returns to the state of common muriatic acid.

The distinguishing chemical characters of oxymuriatic acid are derived from the large quantity of oxygen it contains, the little condensation of that oxygen, and the weak force of affinity by which it it retained. From these circumstances it seldom enters entire into a combination, at least of an energetic kind, but is generally decomposed by the superior attraction exerted either to its acid or to its oxygen. The former of these is exemplified in its relation to alkaline bases, the latter in the actions it exerts on inflammable substances.

In the state of gas it yields its oxygen to almost every inflammable body, and in the greater number of cases with such rapidity as to give rise to the phenomena of combustion. It was early observed that a lighted taper immersed in it is not immediately extinguished, but burns with a dense flame: And it was soon discovered that a number of inflammable substances suspended in it at a temperature of 60° or 70°, take fire and burn. These experiments were diversified by some of the German and French chemists, particularly by Westrumb, Fourcroy, and Vauquelin. If a piece of phosphorus be suspended in it, it inflames and burns with splendour; and sulphur, if it be previously melted, suffers combustion *. A number of

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* When the sulphur is not melted, it is not inflamed by the oxymuriatic acid gas, but is dissolved by it. Dr Thomson, by passing a current of oxymuriatic acid gas through sulphur in powder, found that it was at length converted into a liquid of a fine red colour, which he regards as a compound of oxide of sulphur, and muriatic acid, and has named sulphuretted muriatic acid. It exhales a vapour when exposed to the air, is volatile, tastes acid, and deposites a little sulphur when dropt in water. It effervesces strongly with the alkalis, and is decomposed by the acids †. The younger Berthollet has stated.

† Nicholson's Journal, vol. vi. p. 104.

the metals, and their combinations with sulphur, exhibit similar phenomena. Antimony, arsenic, bismuth, nickel, cobalt, zinc, copper, and others in filings or powder, projected into the gas take fire ; the combustion of some of them, as antimony or arsenic, is even brilliant, and is marked with peculiar coloured flames. Sulphuret of antimony or of mercury, and sulphuretted oxide of antimony, are likewise oxygenized with the emission of heat and light. For the success of these experiments, it is necessary that the gas should be pure, and that the temperature should not be lower than 70° ‡.

These effects afford an excellent illustration of the truth, that elasticity is often superior to a chemical affinity in counteracting a chemical attraction; for although the oxygen be retained by the muriatic acid by a certain force of affinity, yet it is so much condensed, that inflammables or metals combine with it with more facility than when it is in its uncombined elastic form.

The elastic state in hydrogen gas is an obstacle to the rapid action of oxymuriatic acid gas upon it. If indeed the electric spark be transmitted through the mixture of these gases, it is inflamed with detonation. But if the

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some experiments from which he has inferred, that the oxygen does not combine exclusively with the sulphur to form an oxide, but that the acid, oxygen and sulphur merely unite and form a ternary compound. In this combination, he found the usual powers of the oxymuriatic acid to be completely suspended. He names it oxy-sulphuretted-muriatic acid †.

† Crell's Chemical Journal, vol. i. p. 137.

‡ Mémoires de la Société d'Arcueil, tom. i. p. 161.

temperature is not elevated, their mutual action is much more slow. Still, however, the hydrogen gradually receives oxygen from the acid. Mr Cruickshank mixed one part by measure of hydrogen gas, and two parts of pure oxymuriatic acid gas. There was no immediate diminution of volume. But after the mixture had been allowed to stand for twenty-four hours in a bottle which was stopt, on opening it under water, the whole disappeared except about one-tenth of a measure, which was found to be nitrogen that had been accidentally present *. It decomposes in a similar manner, as has been already stated, the different oxycarburetted hydrogen gases, and the carbonic oxide gas †. Sulphuretted hydrogen is decomposed by it, and with phosphuretted hydrogen it produces combustion. Its action on hydrogen in a state of greater condensation is also well shewn in the decomposition which ammonia suffers from it. If they are mixed in the gaseous form, the mixture is accompanied with inflammation, and nitrogen gas is the residuum, the oxygen of the acid combining with the hydrogen of the ammonia, and forming water, by which the muriatic acid is condensed. Or when a current of oxymuriatic acid gas is transmitted through liquid ammonia, there is a disengagement of nitrogen in the elastic form, from the decomposition of the alkali.

It communicates oxygen to sulphurous acid, converting it to sulphuric; and nitric oxide gas, it changes to nitrous acid vapour.

When the oxymuriatic acid is combined with water,-

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* Nicholson's Journal, 4to, vol. v. p. 202. † Ibid. p. 204.

as the affinity between its elements is strengthened by the affinity which the water exerts to them, its action on inflammable substances, which depends on its parting with oxygen, is less energetic. It slowly oxidizes phosphorus; on sulphur in its usual state of aggregation it scarcely acts; but when in the state of sulphuretted hydrogen dissolved in water, it affords oxygen to its principles. It is rather more active with regard to the metals; it oxidates them, and the metallic oxide remains in combination with the muriatic acid, into which the oxymuriatic is converted; and as the oxygen in the oxymuriatic acid is not retained by a strong force, even those metals which in general attract it least powerfully, as gold, are oxidized and dissolved by the acid. Very little heat attends these actions, and no emission of light, a fact which has been regarded as a proof of the identity of heat and light, and that the latter may be disengaged under the form of caloric.

The most important property of this substance, that of destroying the vegetable colours, probably likewise depends on the peculiarity in its constitution, now illustrated,—the large quantity of oxygen it contains, not much condensed, and not retained by a strong attraction. Oxygen appears to have the property of destroying the colour of vegetables, by combining with the principles in which it resides, as is exemplified in the process of etiolation, and in the old method of bleaching; and being afforded by the oxymuriatic acid, enables it to produce this effect.

This property is displayed by it either in its gaseous form, or combined with water. If the gas be transmitted through any vegetable infusion or solution of a blue, purple, red, or green colour, or if any vegetable coloured matter be exposed to it, the colour is immediately discharged, or, if it has been a deep and permanent colour, becomes of a faint yellow. The same effect is produced on adding the solution of the oxymuriatic acid in water.

On this property is founded its application to the art of bleaching linen and cotton, an application now established, and from which important advantages are derived, the new process being performed with much celerity, saving, therefore, much capital, being attended with less labour, and being capable of being executed in all situations, and at all seasons of the year, while, if properly managed, the texture of the thread or cloth sustains no injury. To Berthollet we are indebted for what may justly be termed a new chemical art. He first applied the agency of the oxymuriatic acid to this purpose, and gave the details of the process *. Since then it has undergone various improvements. In this work a general outline only can be given of it.

The art of bleaching consists, not merely in discharging the colour of the thread, but likewise in removing the colouring matter itself, as otherwise a sensible shade would be regained. In the old method of bleaching, this was attained by alternate exposure of the thread or cloth to the action of light, humidity, and atmospheric air, and of an alkaline lye, the cloth being macerated in a solution of potash, exposed on the field to the air and sun, and frequently sprinkled with water, and these alternate practices being continued until the bleaching was complete.

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* Annales de Chimie, tom. ii. p. 151, tom. vi. p. 204. or, Translation of these Memoirs, by Kerr.

In the new method, the action of the oxymuriatic acid is substituted for that of the light, air, and water; and it answers the same purpose, by affording oxygen to the colouring matter, thus impairing the colour, and probably rendering the matter soluble in the alkaline solution.

At first this process was performed by exposing the cloth to the action of the acid in the state of Gas; but this was found to act unequally on the cloth, the texture being injured in one part, while in another it was imperfectly whitened. The solution of it in water was substituted, and even this requires to be considerably diluted.

The acid or bleaching liquor, according to the directions given by Berthollet, is prepared by putting 6 parts of black oxide of manganese, and 16 of muriate of soda, into a glass, or earthen retort, or a leaden bottle, and pouring upon them 12 parts of sulphuric acid, diluted with 9 of water. The retort or bottle is connected by a tube with a receiver, designed to retain any common muriatic acid that may pass over; from this vessel another tube issues, which is inserted in a large wooden cask filled with water. The tube descends nearly to the bottom of the cask, so that the gas has to rise through the whole body of the water; at the same time, the absorption of it is promoted by the motion of a circular frame placed in the middle of the cask, and which can be turned round at the top. The oxygenated acid is thus easily condensed. After the first disengagement of the gas has ceased, heat is applied to the retort, by placing it in a sand bath, or if a leaden bottle be used, by placing it in a vessel of boiling water. So much water is used, that the oxygenated acid is very weak; it requires to be stronger for coarse than for fine cloth, and for linen than for cotton; the average quantity stated by Berthollet, is 100 quarts for every pound of muriate of soda that has been used.

The cloth to be bleached is prepared by macerating it in warm water, for some hours, to take up what part of the colouring matter may be soluble. It is then boiled in an alkaline ley, prepared from 20 parts of water, and one part of the potash of commerce rendered more active by having been mixed with one third of lime. After sufficient boiling it is washed with water, and put into close wooden troughs, containing the oxygenated acid, in which it is allowed to macerate for 3 or 4 hours, pressing the cloth frequently, and exposing its surfaces to the action of the liquor. It is thus alternately exposed to the action of the alkaline ley, and the oxygenated acid, till its colouring matter is completely extracted, or it is sufficiently bleached, which requires in general from 4 to 8 immersions, according to the nature and coarseness of the cloth, cotton requiring fewer immersions in the bleaching liquor than linen.

The subsequent steps of the process are to rub the cloth strongly with soft soap in warm water. This renders the surface more smooth and uniform, and takes away the smell of the oxygenated acid, which otherwise remains a considerable time. The cloth is again washed, and is lastly immersed for a short time in water, in which, from a one-sixtieth to a one-hundredth part of sulphuric acid has been dissolved. It thus acquires a much finer whiteness, from the sulphuric acid dissolving the remaining colouring matter which has resisted the action of the alkali and oxygenated acid, as well as a small quantity of iron and calcareous earth contained in all vegetable matter, or deposited in the cloth from the alkaline leys. Lastly, the cloth is generally exposed to the air for some days, and watered, to carry off any remains of either of the acids, and to remove completely the odour of the oxygenated acid.

Several alterations have been made in the process since it was introduced, and it is now practised in this country in a method different from that above described.

The greatest difficulty attending the use of oxymuriatic acid arose from its suffocating odour, which rendered it almost impossible to work with it in an open vessel, and any apparatus contrived to turn the cloth and expose fresh surfaces of it to the action of the liquid in close vessels, has been found imperfect *.

The addition of an alkali to the liquid, removes in a great measure the odour of the acid, or at least prevents its unpleasant effects; and although it at the same time diminishes to a certain extent its bleaching power, this is more than compensated for by this advantage. The quantity of alkali which was added, amounted to about 1 lb. of the potash or pearl-ash of commerce to the quantity of acid prepared from 4 lbs of muriate of soda. And to avoid the effervescence which would arise from the disengagement of the carbonic acid during the combination of the oxymuriatic acid, the potassa is deprived of it by the pre-

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* That invented by Mr Rupp, and described in the Manchester Memoirs, vol. v. is probably the best, but even it has not been established in use.

vious addition of lime, the alkaline solution after its operation being poured off clear.

Independent of the weakening of the power of the acid by this addition, a considerable expence was introduced by the use of the alkali; and it became an object of importance to the manufactures of this country, to substitute a cheaper substance which should have the same effect. Lime was tried, at first in an imperfect manner, but at length with such improvements that it is now always used.

The difficulty of using it arose from the insolubility of the lime in water, the quantity taken up being so inconsiderable, that the solution could have little effect in correcting the odour of the acid. An important improvement, therefore, was that of using lime suspended in water, and kept in suspension by an agitator in a close vessel, into which the gas was transmitted. Its condensation was thus facilitated, and the compound which it formed with the lime being soluble in water, the undissolved or unsaturated lime was allowed to subside, and the clear liquor was fit for bleaching. Where the manufacturer himself prepares the liquor this is the most advantageous method. The proportions given by Mr Tennant in the specification of the patent he obtained, were 60 lbs. of lime suspended in 140 gallons of water, or rather, on account of its greater specific gravity, a solution of salt; this being exposed to the gas from 30 lbs. of oxide of manganese, 30 lbs. of sea-salt, and 30 lbs. of sulphuric acid previously diluted with its bulk of water.

An improvement of still more importance has been made by Mr Tennant of Glasgow, and a patent obtained for it, that of combining the oxymuriatic acid with dry lime, and dissolving a certain proportion of this compound in water to form a bleaching liquor. It perhaps could scarcely have been supposed *à priori* that such a combination could have been formed, so as to retain the powers of the acid. But the trial succeeded, and the advantages derived from it are important; the compound can be carried easily to a distance, and the manufacturer need not prepare it himself, which is always an advantage, where he does not work on a large scale. The combination is formed by introducing the oxymuriatic acid gas through leaden tubes into slaked lime prepared from chalk, by which it is absorbed. Solutions of this are prepared of different strengths according to the purposes to which they are to be applied, the strength being judged of by the hydrometer, and by the quantity requisite to destroy the colour of a diluted solution of indigo in sulphuric acid.

The process of bleaching, as now performed by these liquors, differs little from that which has been already described as executed by the solution of the oxymuriatic acid alone in water. The practical details of all that relates to it, will be found in the Art of Bleaching by Pajot des Charmes, translated by Mr Nicholson.

The theory of the action of the oxymuriatic acid in bleaching is very simple, as stated by Berthollet. Its analogy to the common process, by exposure to the air and light, he observes, is complete. The end obtained by either, is the combination of oxygen with the colouring matter, this being yielded by the oxymuriatic acid in the new process. It is accordingly found, what is conformable to this view, that the oxymuriatic acid is converted into muriatic acid, the liquid at the end of the operation precipitating nitrate of silver, a property belonging to muriatic and not to oxymuriatic acid. By this oxygenation of the colouring matter, the colour is destroyed; in time, however, a tint of colour would be regained, and hence, in the process of bleaching, the advantage of the alternate application of an alkaline solution, by which the colouring matter, rendered more soluble, probably by its oxygenation, is abstracted.

It has accordingly been discovered, that the alkali itself, when aided by a high temperature, and the solvent power of water, is capable of dissolving the colouring matter; and this either alone, or combined to a certain extent with the method by the oxymuriatic acid, is now practised with much advantage. In this method, which has been long in use in some of the eastern countries, and of which notice was first given by Chaptal, the cloth or thread is impregnated with a solution of potassa or of soda, rendered active by the carbonic acid having been entirely abstracted from the alkali by lime; it is suspended loosely, and with an extensive surface, in a close boiler, a quantity of the same solution being in the bottom, and heat is applied, the boiler being closed, with a safety valve in the cover, so that the vapour under pressure may receive a high temperature. It is kept in this situation for a number of hours. The thread or cloth when cold is washed, and either exposed on the field, or subjected to the action of the oxymuriatic acid in one or other of the forms under which it is used. It is thus at once rendered perfectly white. The superiority of this method probably arises from the high temperature, and the solvent power of the watery vapour, favouring the action of the alkali on the colouring matter, while this vapour penetrates the fibres of the cloth, so effectually, that that matter is in a great measure dissolved and removed[*]. The process has every advantage over the old method in facility of execution, in celerity, and diminution of expence; nor does the strength of the fibre appear to be at all injured. The application of this method to cleansing linen in hospitals and similar institutions may be regarded too as one of considerable value. On this subject the details given by Chaptal in the memoir quoted beneath, deserve to be consulted.

The oxymuriatic acid has been used from its bleaching power in the manufacture of paper; either the linen rags from which the paper is to be made being bleached by it, or, what has been regarded as preferable, the pulp into which they are reduced being submitted to its action[†]. This method, though once extensively practised in this country, has been relinquished by many of our paper manufacturers, as it has been found that in paper prepared with it, in the course of a few years, the ink is altered, and its blackness even so much impaired, as to afford some reason for the suspicion that in time it will altogether fade; nor is this confined to writing ink, but has been observed even in printing ink. The effect is no doubt to be ascribed to a slight impregnation of the oxymuriatic acid; and this indeed can often be rendered perceptible, by its odour, by breathing on paper which has been bleached in this mode. It might be removed by very careful washing of the pulp, but I have been informed by some intelligent paper manufacturers, that the additional labour requisite for this, would upon the whole render the method more expensive than the old one. The process of bleaching by steam with an alkali at a high temperature, might probably be advantageously employed.

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[*] Nicholson's Journal, 4to, vol. iv. p. 469. vol. v. p. 233. Philosophical Magazine, vol. x. p. 305.

[†] Nicholson's Journal, 8vo, vol. i. p. 118.

A branch of the manufacture, however, in which the acid necessarily must be used, is that of discharging the colours from coloured rags, or to remove the ink from waste written paper. Even printed paper has been whitened by its agency combined with that of an alkali to remove the oily matter, and made to afford at least a coarser kind of paper. On this tubject there are some observations in the work of Pajot des Charmes, and in the dissertation on bleaching by O'Reilly *. Chaptal applied it to the purpose of restoring the colour of old books or prints, the paper being whitened by a very dilute acid, which did not act sensibly on the printing ink. From the preceding facts the propriety of this practice may be doubted.

Wax reduced to thin plates has been bleached by the oxymuriatic acid. The process succeeds best when the acid is used in the state of gas.

Berthollet, some time ago, announced a peculiar effect obtained from the action of oxymuriatic acid, that of giving the appearance of cotton to hemp or flax. The process consists in immersing the flax, prepared by boiling, and by an alkaline solution, in oxymuriatic acid of a certain strength for some time, and alternating this immersion repeatedly with the action of an alkaline ley †.

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* Philosophical Magazine, vol. x. p. 313.

† Nicholson's Journal, 8vo, vol. vi. p. 252.

An application of the oxymuriatic acid, dependent probably on the facility with which it parts with oxygen, is that of destroying or neutralizing contagion. On this subject, the treatise of Guyton, "*Sur les Moyens disenfecter l'Air*," may be consulted.

THE peculiar character of the Oxymuriatic Acid, in its chemical relations to other substances, it has been already remarked, depends principally on the weak attraction between its principles, in consequence of which it seldom enters into intimate combinations, but is decomposed from one of its principles being attracted with more force than the other. The preceding agencies depend on its oxygen being attracted. In its relations to the alkalis, we discover phenomena arising from the stronger attraction which they exert to the muriatic acid.

When oxymuriatic acid is added to an alkaline solution, so that the alkali is saturated, a singular kind of action is found to have taken place. Instead of the immediate combination of the oxymuriatic acid and the alkali being established, we find, on evaporation, that a quantity of muriate of the alkali, suppose it to be potassa, is formed, along with another salt containing muriatic acid and a large portion of oxygen, and which is possessed of very peculiar properties. This is a proof that the oxymuriatic acid has been decomposed. Since, from its introduction to the alkaline solution, a quantity of common muriate is formed, it is evident, as Berthollet, who first observed the fact, concluded, that a portion of it must have parted with its oxygen, and returned to the state of muriatic acid; and hence he inferred, that the acid which exists in the other salt likewise formed, has a still larger proportion of oxygen in its composition than what exists in the oxymuriatic acid. This inference is accordingly established by actual analysis. By the experiments already stated, it is proved, that oxymuriatic acid consists of 16 parts of oxygen with 84 of muriatic acid, while the acid existing in the salt formed along with the muriate in the above experiment is composed of not less than 65 of oxygen with 35 of muriatic acid.

This decomposition of oxymuriatic acid by the alkaline bases, whether the pure alkalis, or the alkaline earths, and this formation of an acid, with a still larger proportion of oxygen, is justly ascribed to the attraction of the alkaline base to the muriatic acid being stronger than its attraction to the oxygen, while at the same time the muriatic acid is capable of combining with a larger proportion of oxygen than what exists in the oxymuriatic acid.

From this, it has been inferred, that no such compounds as those of the oxymuriatic acid with the alkalis or earths can be formed, or that no such order of salts as the oxymuriates exists. Mr Chenevix, by whom this subject has been fully and ably investigated, had supposed, that in impregnating an alkaline solution with oxymuriatic acid, the acid remained undecomposed in union with the alkali, until the moment of crystallization; but he changed this opinion, and concluded, that the liquor, even in that state, does not contain any oxymuriate. He admits, however, that oxymuriate of ammonia can be formed, and infers from analogy, that the others may also exist previous to the formation of the hyper-oxymuriates.

The views of Berthollet on this subject appear to be correct. He supposes the nature of the combinations which take place when oxymuriatic acid is presented to an alkaline solution, to be considerably influenced by the concentration of the solution, by which the affinities exerted by the alkali, as well as the affinities between the constituent principles of the acid itself, must be modified.

He first observes, that when the oxymuriatic acid is in a diluted state, the affinity exerted between it and the alkali, or between the muriatic acid it contains and the alkali, is very weak, so much so, that it is even unable to expel carbonic acid from an alkaline carbonate, no effervescence ensuing when the liquid oxymuriatic acid is added to their solution, and the carbonate of lime being even dissolved entire by it. But if it be passed in the state of gas into a solution of carbonate of soda or potassa, the carbonic acid is disengaged from the oxymuriatic acid gas in its immediate absorption by the liquid, being in a more concentrated and dense state in the parts with which it comes in contact *.

When the oxymuriatic acid is passed into a solution of potassa a little concentrated, and when much of the acid is condensed, a part of it is decomposed; but instead of being entirely resolved into the muriatic and what has been named the hyper-oxymuriatic acids, it gives out part of its oxygen, which assumes the elastic form. This had been observed by Berthollet; but Chenevix having supposed that he might have been deceived by a portion of carbonic acid which remained with the alkali, the former

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* Chemical Statics, vol. ii. p. 164.

chemist repeated the experiment, and found that much oxygen gas is disengaged, even in the dark, a proof that it is not owing to the chemical agency of light *.

But besides this decomposition of the oxymuriatic acid, this reproduction of muriatic acid, formation of hyper-oxymuriatic acid, and disengagement of oxygen gas, there takes place, as Berthollet has supposed, a simple combination of the oxymuriatic acid with a portion of the alkaline base. There is a plain, and apparently decisive proof that this opinion is just. An alkaline liquor which has absorbed the oxymuriatic acid, has the property of destroying the vegetable colours in a greater degree even than a solution of the oxymuriatic acid in water alone. Now this must be owing to a portion of oxymuriatic acid being present in it; for the hyper-oxymuriates, it is established by experiment, have little or no power of this kind; and that it is not owing to a portion of oxymuriatic acid being contained in the liquor in excess, or unsaturated, is proved by this, that the solution has the power of destroying the vegetable colours, even where there is an excess of alkali. But it could not have such a power, were the whole of the acid converted into muriatic and hyper-oxymuriatic acids, with which the alkali unites, and the property retained by it proves the presence of oxymuriatic acid in union with the alkali. Another fact leading to the same conclusion is, that an alkaline solution impregnated with oxymuriatic acid is decomposed by light. As there may be in the liquid; without preventing this result of the experiment, an excess of alkali, there

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* Chemical Statics, vol. ii. p. 165.

can be no free oxymuriatic acid to be decomposed; the hyper-oxymuriatic acid, in combination with an alkaline base, it has been ascertained, suffers no decomposition from light; and the disengagement of oxygen gas, which Berthollet has found does take place, must arise from the decomposition of the portion of oxymuriatic acid in combination with the alkali, and is, of course, a proof of the existence of such a combination.

These combinations of oxymuriatic acid with alkaline bases, though their existence is proved, cannot be obtained pure and insulated, as there is probably always formed at the same time with the oxymuriate an hyper-oxymuriate, and any operation which could be had recourse to to obtain the former apart, will probably give rise to the exertion of new affinities by which it will be changed. Berthollet has shewn even that the gradual transition of the oxymuriate in a state of solution into the hyper-oxymuriate takes place; for having impregnated an alkaline solution with oxymuriatic acid, he divided it into two portions, one of which was immediately exposed to the light, while the other, before being exposed, was kept in darkness for 15 days; the quantity of oxygen given out by the former was to that from the latter as 16 to 7, a difference to be ascribed to the gradual transition of the oxymuriatic to hyper-oxymuriatic acid, by the continued action of the base.

The properties of the oxymuriates, therefore, farther than what has now been stated, are unknown.

SECT. III.

OF HYPER-OXYMURIATIC ACID.

The formation of this acid, in presenting oxymuriatic acid to an alkaline base, has been explained in the preceding statement. This is the only mode in which it can be produced; nor is it easy to separate it from the combinations into which it passes at its formation, so as to obtain it in a pure and insulated state. By pouring sulphuric acid on the salt it forms with potassa, a dense vapour arises of a greenish yellow colour, and of a strong fœtid odour, different from that of the oxymuriatic acid; the liquor around the salt at the same time acquires an orange colour. But though in this experiment the hyper-oxymuriatic acid is disengaged, it is not pure, as the affinities which effect its disengagement subvert partially its composition, and convert a part of it into oxymuriatic acid. Nor is it possible even to obtain this elastic fluid so as to submit it to accurate examination, as its disengagement is in small quantity, and the application of heat to favour it immediately causes an explosion. If the sulphuric acid be diluted, heat may be applied with more safety; but at the temperature thus produced, the conversion of the acid into oxymuriatic acid, and the evolution of a portion of oxygen, take place. Nitric acid produces nearly the same phenomena; the muriatic acid decomposes the acid of the salt still more completely; and the other acids, which require heat to enable them to act on it, always occasion more or less decomposition, and consequent evolution of oxygen.

This acid is therefore better known to us in its saline combinations, especially since the able investigation of them by Mr Chenevix *, and it is to an account of these that its history must be in a great measure confined. They are named Hyper-oxymuriates, and from the peculiarity of their chemical composition,—the large quantity of condensed oxygen existing in them, and retained by no strong attraction, their characters are extremely distinctive. The principal are, affording very pure oxygen when exposed to a red heat, detonating with great violence with inflammable bodies, either on the application of heat or by mere percussion or trituration, and causing such bodies to burn when sulphuric or nitic acid is added to the mixture of the salt and the inflammable matter. They decrepitate on mere trituration. Their taste is cool and penetrating; they are generally soluble in water, and crystallizable; the greater number of them are also soluble in alkohol. They do not precipitate any of the metallic salts. They do not destroy the vegetable colours; but rather in small quantity heighten their brilliancy.

From the decomposition of these salts by heat, Mr Chenevix endeavoured to determine the proportions of oxygen and of muriatic acid in the hyper-oxymuriatic acid; 100 grains of hyper-oxymuriate of potassa were raised to a temperature near to that of ignition, in a coated glass retort, connected with a dry receiver, from which a tube issued, communicating with a jar in the pneuma-

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* Philosophical Transactions, 1802.

tic trough; the salt by the first application of heat was previously found to lose 2.5 *per cent.* from the escape of water; when nearly at a red heat, oxygen gas was disengaged, which amounted to 38.3 grains, and the residual salt weighed 58.5 grains. This salt, decomposed by nitrate of silver, gave a precipitate, which in quantity corresponded to 20 of muriatic acid. Hence 38.3 of oxygen, and 20 of muriatic acid, combine to form 58.3 of hyper-oxymuriatic acid, or 100 parts of this acid consist of 65 oxygen, and 35 muriatic acid.

HYPER-OXYMURIATE OF POTASSA.—To prepare this salt, 4 parts of sub-carbonate of potassa are dissolved in 16 of water, and 2 parts of lime are added to the solution to abstract the carbonic acid. The solution of potassa being obtained clear by filtration, is put into the bottles of Woulfe's apparatus, and connected with a retort containing a mixture of muriate of soda, black oxide of manganese, and sulphuric acid, in the proportions already stated for forming oxymuriatic acid. The first bottle of the apparatus is left empty, to condense a little muriatic acid that passes over, holding a portion of oxide of manganese in solution. By the application of heat, the oxymuriatic acid continues to be disengaged; and passing through the solution of potassa, suffers the decomposition that has been already described, and the theory of which has been explained; one part passes to the state of muriatic acid, which forms muriate of potassa; another portion, receiving the oxygen which the other had parted with, is converted to the state of hyper-oxymuriatic acid, and this entering into combination with the remaining alkali, forms the hyper-oxymuriate of potassa. The two salts exist in the liquor, but are obtained in a great measure separate by the difference in their solubility; the hyper-oxymuriate being sparingly soluble in water, crystallizes as the saturation proceeds, when a solution of potassa of the above strength has been employed, and collects in scales at the bottom of the bottle; the muriate of potassa remains in solution. At the end of the process, the whole is poured out, the hyper-oxymuriate is washed with a small quantity of water, and allowed to dry. Part of it remains in solution in the liquor, and probably also a portion of oxymuriate, as it is capable of discharging the vegetable colours; a salt even is obtained by evaporation, which is probably of this nature, Mr Hoyle, to whom we are indebted for some excellent observations on these combinations *, having remarked, that although it does not detonate like the proper hyper-oxymuriate with sulphur, yet, " with the addition of sulphuric or muriatic acid, it becomes a very powerful destroyer of vegetable colours." It is not practicable, however, by evaporation of the remaining liquid, to obtain hyper-oxymuriate pure; and hence the portion only is collected which crystallizes spontaneously.

The salt obtained in this way is in the form of small brilliant scales or thin quadrangular plates, white, and of a silvery lustre. By a slow spontaneous evaporation, it crystallizes, as Hoyle observed, in needle-like crystals. Its taste is cool and penetrating. It requires about 17 parts of water at the temperature of 60 for its solution, while

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* Manchester Memoirs, vol. v.

its solubility is so much increased by augmentation of temperature, that five parts of boiling water dissolve two parts of it. In crystallizing from this solution, it becomes whiter than it is at its first formation, and deposites a small quantity of earthy matter, probably derived from the impurity of the alkali.

Hyper-oxymuriate of potassa is fused by a moderate heat, losing a little weight from the escape of its water of crystallization. By raising the heat nearly to ignition, its acid is decomposed, and very pure oxygen gas is expelled, amounting to more than one-third of the weight of the salt. From this decomposition, and from the quantity of muriatic acid which remains in combination with the potassa, Mr Chenevix endeavoured to determine, as has been already stated, both the proportions of the constituent principles of the salt, and those of its acid. 100 grains of it, freed from its water of crystallization, yielding 38.3 of oxygen, and the residuum containing 20 of muriatic acid, it follows, that its ultimate elements are 38.3 of oxygen, 20 muriatic acid, and 39.2 potassa, or, as the two former constitute the hyper-oxymuriatic acid, that its immediate constituent principles are, hyper-oxymuriatic acid 58.3, potassa 39.2, and water of crystallization 2.5.

Hyper-oxymuriate of potassa Mr Hoyle found, contrary to the assertion of Chaptal, is not decomposed either in its concrete state, or in solution in water, by the agency of light, the resulting affinity of the base preserving the constitution of the acid.

When subjected to mere trituration, it appears to undergo some decomposition, as it gives slight decrepitations, and flashes of light visible in the dark.

This salt is decomposed by the acids, decompositions which have been examined by Hoyle, and afterwards by Chenevix. If a ſew grains of it be thrown into concentrated sulphuric acid, a number of small explosions or decrepitations take place, accompanied sometimes with flashes of light; the liquor around the salt acquires an orange or red colour; and a dense yellow vapour, having an oppressive smell, floats above. This is hyper-oxymuriatic acid mixed with oxymuriatic acid gas. If heat be applied, an explosion, with a white and vivid flash, always takes place, as Mr Chenevix found, when the liquid has attained the temperature of 125°, and accidents have repeatedly happened from making this experiment. The explosion even happens, Mr Hoyle found, when the acid is a little diluted with water. If it is more diluted, a wide-necked retort used, and the heat is cautiously applied, the action is more moderate; the hyper-oxymuriatic acid is decomposed, and appears to be converted principally into muriatic acid and oxygen; the production of the first was observed by Hoyle; of the second with a portion of oxymuriatic acid by Chenevix. If the concentrated sulphuric acid, and the salt, be allowed to stand for some days without the application of heat, oxygen gas continues to be disengaged.

The action of nitric acid on hyper-oxymuriate of potassa is similar to that of sulphuric acid, only less violent.

Muriatic acid is converted into oxymuriatic acid, by receiving the excess of oxygen of the hyper-oxymuriatic acid, and passes in part to the elastic state. A few grains of the salt, added to an ounce of muriatic acid, give it the property of destroying the vegetable colours.

When inflammable substances are presented to the hyper-oxymuriatic acid disengaged from its combination by sulphuric or nitric acid, it acts on them with the utmost energy; brilliant combustions are exhibited, and the experiments can indeed be properly made only on small quantities of the materials. If five or six grains of the salt be mixed with two or three grains of sugar, and be thrown into a little sulphuric acid, there is instantly a vivid combustion; or if the salt in powder be made into a soft paste with any essential or fixed oil, it is inflamed in a similar manner. The same phenomena are exhibited with camphor, resins, charcoal, sulphur, and other inflammables. The experiment may even be managed so as to cause some of them to burn under water. Even touching the mixture of the salt and the inflammable matter with a rod dipt in sulphuric acid, is sufficient to inflame it. With nitric acid, the effects are similar, but less violent. These phenomena are owing to the acid disengaging from the salt the hyper-oxymuriatic acid, which immediately affords oxygen in a very dense state to the inflammable matter, and enables it to burn.

The action of hyper-oxymuriate of potassa alone on inflammable substances, when promoted by mere compression, as by trituration or percussion, is extremely violent, so as to prevent the experiment from being made with more than a few grains of the materials. A number of experiments of this kind were made by Fourcroy and Vauquelin, and by Mr Hoyle, who have given the different proportions to be used, and their effects *. A grain

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* Nicholson's Journal, 4to, vol. i. p. 168, and vol. ii. p. 294.

of the salt with half a grain of sulphur rubbed in a stone mortar decrepitates strongly, or if struck on an anvil gives a loud report with a flash of light. Two grains with one of charcoal give a strong flame. Half a grain of phosphorus, covered with about the same quantity of the salt, and struck, gives a report extremely loud, and small particles of the phosphorus are projected with violence, so as to render the experiment somewhat dangerous, at least if any larger quantities than these be used. Antimony, arsenic, zinc, and a number of metallic sulphurets, fulminate when mixed with the salt, and struck with a smart blow; and similar phenomena are produced by many inflammable substances, both solid and liquid.

These mixtures are likewise inflamed by the electric spark, and by the application of heat. Some of them, that for example of the salt with arsenic, inflame with such violence as to render the experiment dangerous.

These phenomena arise from the rapid combination of the oxygen of the hyper-oxymuriatic acid with the inflammable body, and the instantaneous formation of a product, either rendered elastic, or having its elasticity augmented, by the large quantity of caloric which has been retained by the oxygen in its condensation, and which is set free by the new combination. What confirms this explanation is, that of the metals, those only detonate when struck with the salt, which are volatile. The effect of the mechanical compression is to be ascribed to its suddenly approximating the particles of oxygen, and of the inflammable matter, and perhaps also favouring their union by the slight momentary elevation of temperature which it must produce. This is the general theory of detonations from percussion, and the violence of those produced with the hyper-oxymuriates arise from the large quantity of concrete oxygen in their composition, and the weak affinity by which it is retained.

From this property of the hyper-oxymuriate of potassa, it was an obvious idea, that it might perhaps be employed for the preparation of a powerful gunpowder. The experiment made under the direction of Lavoisier at Essone in 1788, must for ever preclude such a trial, the materials having exploded during the trituration, and two individuals having lost their lives. It is not even altogether safe to keep a mixture of this salt with an inflammable substance in any quantity, as a very slight agitation is sufficient sometimes to cause it to explode.

This salt is used in chemistry to obtain oxygen gas, in experiments where it is of importance to have oxygen perfectly pure.

Hyper-oxymuriate of Soda.—This salt is prepared in the same manner as the preceding, but it is much more difficult to obtain it pure, as it is nearly of the same degree of solubility in water as muriate of soda, which is necessarily formed along with it when the current of oxymuriatic acid gas is transmitted through a solution of soda. Mr Chenevix obtained it by treating with alkohol the entire salt formed in that process; the hyper-oxymuriate, by repeated solution in that fluid, and crystallization from it being obtained pure; and he is the only chemist who has examined it. It is soluble in three parts of cold, and less of warm water; is slightly deliquescent, crystallizes in cubes, or rhomboids little different from cubes. Its taste is cool. It is decomposed by heat; and its relations to the acids, and to combustible bodies, are similar to those of the preceding salt. According to the analysis of it by Mr Chenevix, it consists of hyper-oxymuriatic acid, 66.2 parts; soda, 29.6; and water, 4.2.

HYPER-OXYMURIATE OF AMMONIA.—The formation of this salt might be thought impossible, as ammonia is decomposed when presented to oxymuriatic acid gas. Though it cannot be produced by the usual process, Mr Chenevix succeeded in obtaining it, by pouring a solution of carbonate of ammonia into the solution of a hyper-oxymuriate, having lime or some other earth for its base; a double decomposition ensued, and hyper-oxymuriate of ammonia was formed. This salt is described by this chemist as very soluble in water and in alkohol: It is decomposed at a low temperature, giving out a quantity of gas, and a smell of hyper-oxymuriatic acid. The proportions of its principles could not be ascertained.

HYPER-OXYMURIATE OF BARYTES is obtained according to the general process given by Chenevix for the preparation of the earthy hyper-oxymuriates,—passing oxymuriatic acid gas through water in which the earth is diffused; hyper-oxymuriate and muriate of barytes are formed; the latter is abstracted by boiling the solution with phosphate of silver, dissolved in distilled vinegar: this decomposes it, forming phosphate of barytes and muriate of silver, which are both precipitated, while the hyper-oxymuriate of barytes remains dissolved. Mr Chenevix merely remarks of it, that it has the general properties of the hyper-oxymuriates, and that it consists of 42.2 of base, 47 of acid, and 10.8 of water.

HYPER-OXYMURIATE OF STRONTITES is prepared by a similar process. It crystallizes in needles, is deliquescent, and soluble in alkohol. It consists of 26 of base, 46 of acid, and 28 of water.

HYPER-OXYMURIATE OF LIME is extremely deliquescent, liquefies at a moderate heat, from the influence of its water of crystallization, and is very soluble in alkohol. It produces much cold, and a sharp bitter taste in the mouth. It is composed of 28.3 of base, 55.2 of acid, and 16.5 of water.

HYPER-OXYMURIATE OF MAGNESIA, in its general properties, approaches to that of lime. It consists of 25.7 of base, 60 of acid, and 14.3 of water.

HYPER-OXYMURIATIC ACID dissolves argillaceous earth, but the salt cannot be obtained in an insulated state. Its compounds with glucine, zircon, and ittria, are not known.

IN concluding the history of the combinations of muriatic acid with oxygen, I may take notice of a compound acid, analogous to the oxymuriatic, and related to it,—that which is formed by the mixture of muriatic and nitric acids, and which has been named the NITRO-MURIATIC, known to the older chemists by the name of Aqua Regia, from being the most powerful solvent of gold, which, in the language of the alchemists, was named the king of metals.

When these two acids are mixed together, in the proportion of one part of muriatic to two of nitric, the temperature rises, the mixed fluid acquires a deep orange, or even a red colour ; the smell of oxymuriatic acid becomes strong, and at length an effervescence from the disengagement of an elastic fluid takes place. A similar compound is formed by adding a muriate, such as muriate of ammonia, to nitric acid.

The gas which is disengaged during the mutual action of these two acids is nitric oxide gas, mixed with oxymuriatic acid, a proof, therefore, that the nitric acid has been decomposed, and a part of its oxygen abstracted. This is transferred to the muriatic acid, forming the oxymuriatic acid disengaged; and the compound acid thus formed consists of muriatic acid, probably of a portion of oxymuriatic acid, and of undecomposed nitric acid surcharged with nitric oxide.

The formation of the oxymuriatic acid in this process is not owing simply to the superior affinity of muriatic acid to oxygen, for when nitric oxide gas, and oxymuriatic acid gas are mixed, the nitric oxide actually takes oxygen from the oxymuriatic, and red vapours of nitrous acid are formed. It is in part owing to the affinity of nitric acid to nitric oxide. Hence as soon as nitric oxide is formed in as large quantity as the liquid can hold dissolved, the farther decomposition ceases, though there may be a portion of nitric acid still undecomposed, and although a fresh quantity of muriatic acid be added.

Nitro-muriatic acid, then, consists of nitric and muriatic acid, with nitric oxide, and probably a quantity of oxymuriatic acid. Conformable to this composition, when an alkali is added, it combines with the two acids, and disengages the nitric oxide.

The peculiar action of this acid on the metals has been ascribed to the oxymuriatic acid believed to exist in it; but, according to Berthollet, it depends on the facility of decomposition of the nitric acid, aided by the affinity of the muriatic acid to the metallic oxide,—the metal receives oxygen from the nitric, and the oxide combines with the muriatic acid; the affinity of the latter promotes the decomposition of the former, and consequently the oxidizement and solution of the metal. It is used in some operations on the metals, particularly in assaying.

CHAP. VI.

OF FLUORIC ACID.

FOR the discovery of this acid we are indebted to Scheele. It is a constituent part of the fossil known to mineralogists by the name of Fluor Spar, being combined in it with lime; it was from this native combination that Scheele obtained it, and by a series of admirable experiments, demonstrated that it is a peculiar acid different from every other.

Though the compound of fluoric acid with lime exists in considerable quantity in nature, the acid had scarcely, until very lately, been known to exist in any other fossil. Klaproth has discovered it, however, in the Saxon topaz. The discovery has been confirmed by Vauquelin, who has found it also in the Brazilian topaz *; and now that

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* Nicholson's Journal, vol. xi. p. 58.

the attention of chemists is directed to it, it is probable that it will be found in other minerals. Mr Davy has indeed already found it in small quantity, in a new fossil, the wavellite*; and it has been found in large quantity in the Chryolite of Greenland. It has also lately been discovered in the animal kingdom. Morichini, an Italian Chemist, in analysing the enamel of the fossil or petrified teeth of the elephant, found it to be principally a combination of fluoric acid and lime. He afterwards detected it in the enamel of the human teeth. And Gay Lussac, prosecuting these researches, found it to exist in ivory†. Mr Brande has given some experiments, however, from which it appears to follow, that no fluoric acid is contained in the enamel,—a glass plate, placed over a mixture of enamel in powder and sulphuric acid to which heat was applied, not being sensibly eroded, which it would have been had this acid been present‡. On the other hand, the discovery of Morichini is stated to have been confirmed by the experiments of Berzelius, who has found fluate of lime, both in the enamel, and in the osseous part of the teeth ||.

The composition of this acid was entirely unknown, and it was only from analogy that it was inferred to be a compound. Its decomposition has now been effected, by the agency of potassium. This substance, introduced into fluoric acid gas, burns, by attracting its oxygen; the

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* Nicholson's Journal, vol. xiv. p. 267.

† Philosophical Magazine, vol. xxiii. p. 264.

‡ Nicholson's Journal, vol. xiii. p. 215.

|| Ibid. vol. xviii. p. 75.

base of the acid combines with the potassa that is formed, or with a portion of the potassium, if this be in excess; and this compound reproduces fluate of potassa by combustion, or by the action of water.

To obtain fluoric acid, one part of sulphuric acid is added to an equal weight of the fluor spar, coarsely pounded, in a lead bason, or matrass,—an effervescence is excited; the sulphuric acid exerting a stronger attraction to the lime of the fluor spar, unites with it, and the fluoric acid is disengaged in the form of gas. This gas may be collected over mercury, on which it does not act.

There is some difficulty, however, in examining it, and subjecting it to experiment, from a singular property belonging to it, that of acting rapidly on siliceous earth, and dissolving it. Hence, as glass is composed of this earth, it is speedily corroded,—and glass vessels cannot be used to confine it, without very soon altering its purity, by contaminating it with siliceous earth. This is the reason why lead vessels are used in preparing it.

It is difficult to obtain this acid free from silex, since that earth generally exists in more or less quantity in the native compounds of it with lime. It is not therefore sufficient to disengage it from these combinations by the addition of sulphuric acid,—the fluoric acid gas must again be saturated, with soda or ammonia, and the salt thus obtained may be decomposed a second time by sulphuric acid, when the fluoric acid may be obtained pure. It is scarcely necessary to observe, that these operations must be performed in metallic vessels. Lead has been the metal generally used, but the fluoric acid acts on it, and even when distilled retains a portion of it combined with it.

A platina vessel would be preferable. The gas is either received over mercury, or, if it is to be condensed, a leaden receiver, containing water, is joined to the matrass by a bent tube.

Fluoric acid exists in the form of gas, which no cold or pressure can condense. It is heavier than atmospheric air. It extinguishes combustion, and is incapable of supporting life; it has a pungent suffocating odour, is corrosive, and possesses the general properties of acids:

Fluoric acid gas has a strong attraction for water; hence, when mixed with atmospheric air, a white cloud is formed from the combination of it with the moisture of the atmosphere. It is not otherwise acted on by atmospheric air, nor by oxygen, nitrogen or hydrogen gas. When absorbed by water, the liquid possesses all the general acid properties; it is corrosive when applied to the skin; when diluted with water, it tastes sour, and reddens the vegetable colours; it emits white fumes, which consist of the fluoric acid in the act of combination with the moisture of the air. At the temperature of boiling water the gas is expelled.

The action of fluoric acid, either in the state of gas, or combined with water, upon inflammable substances, is very moderate. It is equally so upon metals. As none of them can decompose it, so as to obtain oxygen, which is requisite for their solution, those few metals only are dissolved by it which are capable of decomposing the water it contains. The other metals may be combined with it, if they have been previously oxidized.

Fluoric acid combines with the alkalis and earths; the salts thus formed are named Fluates. They are generally deliquescent, and can with difficulty be crystallized. They are decomposed by the sulphuric or muriatic acid, the alkaline fluates are decomposed likewise by lime. In power of saturation this acid exceeds all the others, a given quantity of it saturating a larger quantity of any base. Hence, if the views of chemical affinity already given be just, it must be regarded as the most powerful of the acids; and its less energetic action must be ascribed partly to the weak state of concentration in which it is obtained, and partly to it being incapable of directly affording oxygen.

Fluate of Potassa is obtained by saturating potassa with fluoric acid. It is very soluble in water, and its solution may be evaporated even to the consistence of a jelly, without any crystallization; but when the evaporation is carried to dryness, it appears in a foliated form. By an increase of heat the salt is melted, and its acid at length disengaged, though it is doubtful whether this decomposition is not owing to the attraction of the siliceous earth with which the salt is generally contaminated. The salt is still capable of acting upon silex and glass, especially when assisted by heat, a triple compound being formed by the earth, the alkali, and the acid.

Fluate of Soda exhibits properties very similar to those of the former salt. It is not so soluble in water; by evaporation nearly to the consistence of honey, it affords small oblong crystals. It has a bitter taste, and decrepitates on exposure to a red heat. This salt likewise acts upon glass.

Fluate of Ammonia, when dissolved in water, becomes gelatinous by evaporation; this jelly affords small crystals. These crystals are deliquescent; have a bitter taste; they melt on exposure to heat; and the salt is at length sublimed, though with a partial decomposition. This salt likewise acts upon glass. It is decomposed by the other alkalis, and by lime.

Fluate of Barytes is formed by adding fluoric acid, or a solution of fluate of potassa, to muriate or nitrate of barytes: this salt is considerably more soluble than fluate of lime: hence fluoric acid has been used as a test to distinguish between these earths.

Fluate of Strontites. Fluoric acid scarcely acts on the native carbonate of barytes: added to a solution of the earth in water, it occasions a milkiness from the production of a fluate of sparing solubility.

Fluate of Lime.—This compound exists abundantly in nature, forming the beautiful mineral which has been known by the name of Fluor Spar, and which is often regularly crystallized. When artificially formed, by digesting water impregnated with fluoric acid on lime, it is obtained in a very different state: the solution, even when evaporated to a jelly, does not afford crystals. It is insipid, and insoluble in water. It is phosphorescent from heat,—a property which eminently belongs also to the native fluate. It is fused, by a very violent heat, into a transparent glass.

Fluate of Magnesia.—A gelatinous solution is obtained when magnesia is dissolved in fluoric acid; but the properties of the salt have not been determined.

Fluate of Argil.—The combination of fluoric acid with argil, Scheele observed, does not crystallize, but assumes on evaporation the consistence of a jelly; its taste is acid and astringent.

Fluate of Silex.—The peculiar property of siliceous earth is that of being little, if at all acted on in the humid way by any acid except the Flüoric, and the power of acting on this earth is not less characteristic of this acid. The combination between them is effected, either when the acid in its gaseous state, or combined with water, is brought to act on siliceous earth, or on almost any compound containing it. When fluoric acid is disengaged from fluate of lime, by any other acid, if the experiment be made in a glass-vessel, part of the silex of the glass is always dissolved; or if a little flint in powder has been mixed with the materials, the fluoric acid gas holds, dissolved, a large portion of silex. It retains it in solution, when received over quicksilver; but when presented to water, a considerable part of the silex is separated, and forms a kind of gelatinous matter, retaining a little acid; and the acid, absorbed by the water, has a portion of the earth combined with it. If the pure liquid fluoric acid be kept in a glass-vessel, it in like manner acts slowly upon it; or if digested with quartz or flint in powder it becomes impregnated with silex. From an experiment related by Bergman[*], it appears, that by such a process crystals can be obtained. Some finely pounded quartz had been put into a bottle with liquid fluoric acid, which was put aside, slightly corked. At the end of two years, the liquor having been poured out, there were found concreted at the bottom of the vessel, besides innumerable prismatic spiculæ, thirteen small crystals, of an irregular form, but resembling cubes with the angles truncated. These are said to have had the essential properties of quartz: they do not appear to have been analysed by Bergman, however, so as to determine whether they consisted of pure silex, or of this earth combined with fluoric acid; but, according to Fourcroy, they are fluate of silex, fluoric acid being expelled from them by heat, or by the action of a concentrated acid.

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[*] Chemical Essays, vol. ii. p. 34.

The compound of silex and fluoric acid is decomposed by the alkalis, which precipitate the earth. With a certain portion of alkali, and especially with the application of heat, triple combinations are produced: these are easily formed, by exposing fluate of soda, or potassa, to heat, with siliceous earth; and it is probably a similar compound also that is formed, when fluoric acid acts on glass.

Fluate of silex, in its solid or concentrated state, is decomposed by heat; the acid, probably holding a portion of the earth dissolved, being expelled. The same effect is produced by the action of the strong acids.

The fluoric acid, from its property of corroding glass, has been used for etching or engraving upon it. The glass is covered with a thin coat of wax, or is brushed over with a solution of isinglass in water; and when this is dried, figures of any kind are easily traced and cut out, by a graver. It is then covered with the liquid fluoric acid, or, what is preferable, is exposed to the action of the acid in the state of gas; the parts of the glass thus exposed are soon eroded; the impression being more or less deep, according to the time during which it is exposed. Such a method, were it possible to obviate completely the defect, from the brittleness of glass, has, from the hardness of that substance, the important advantage over copper, that the impressions do not become less delicate from the fineness of the lines being diminished by the repeated pressure in throwing them off. Different methods have been proposed to render the method practicable*, and engravings, though not of much delicacy, have even been taken.

CHAP. VII.

OF BORACIC ACID.

THIS acid is comparatively a rare production of nature. It has been found in small quantity in some lakes in Tuscany, and as a constituent part of a fossil in which it is united with lime and magnesia at Luneburg in Hanover; but the source from which it has always been obtained, is a native combination of it with soda, the borax or tincal of commerce, a salt found in Thibet, and which has long been imported into Europe for certain uses to which it is applied.

To obtain the boracic acid from it, two processes are followed. If the borax be dissolved in hot water, and half its weight of sulphuric dropt into the solution, on cooling, small soft scales are deposited, and by evaporation a still larger quantity is procured. These are the boracic acid, the sulphuric acid having combined with the

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[*] Nicholson's Journal, 4to, vol. ii. p. 60.
Philosophical Magazine, vol. xvii. p. 357.
Journal de Physique, tom. xxxii. p. 419.

soda of the borax; they are washed with cold water to carry off any adhering sulphuric acid or sulphate of soda, and are dried. Another process is to dilute one part of sulphuric acid with an equal weight of water, and add it to two parts of borax in powder, in a retort. On applying a moderate heat, the boracic acid is sublimed with the watery vapour, and the greater part of it condenses in scales in the neck of the retort. By this latter process a small quantity of the acid only is procured; and by the former it is not obtained in a state of purity, portions both of the base with which it was united, and of the acid by which it is precipitated, adhering to it. It will probably be obtained purer by employing nitric acid in its precipitation, and afterwards exposing it to a red heat.

The composition of this acid has lately been discovered by Mr Davy's researches. Its principles are separated both by the application of galvanism, and by the action of potassium. When ignited in a gold tube with potassium, a black substance which became white on exposure to the air was produced; and more lately it has been stated, that the base procured by being combined with oxygen reproduces boracic acid.

Boracic acid is in the form of brilliant white scales, soft, and somewhat unctuous to the touch; its taste is bitterish, with a slight degree of sourness; it reddens the vegetable colours. It is not altered by exposure to the air; is soluble in 20 parts of cold water, and in 5 of boiling water. It is also soluble in alkohol, and, what is a very distinctive character of it, gives to the flame of the alkohol in burning a green colour.

Exposed to a moderate heat it swells up; when the heat is raised to redness, it is fused into a glass, which remains transparent for a considerable time; when cold, it retains all its acid properties, and is soluble again in water. By the most intense heat it is not volatilized; but if a small quantity of water be present, the aqueous vapour carries along with it a considerable portion of the acid. It is from this strong attraction between it and water, that it is practicable to obtain it by sublimation, according to one of the processes above described. From the facility with which this acid is fused, and brings other bodies, particularly the earths, into fusion, it is of much use in analyses performed by the blow-pipe.

Boracic acid combines with the alkalis and several of the earths, forming compounds named Borates in the new nomenclature. These salts retain in general the property of communicating a green colour to the flame of alkohol. They are decomposed by all the acids, the carbonic excepted, in the humid way. In the dry way, however, the boracic acid, from its great fixity, is able at a high temperature to decompose several of those salts, in which the acid of which they are formed has a tendency to assume the gaseous form. Its attractions appear stronger to the earths than to the alkalis. The alkaline borates are very soluble in water, while the earthy are the reverse.

Borate of Potassa.—This salt is prepared by the direct union of its principles; its properties are very little known. It has a tendency to attract an excess of alkali; it is soluble in water; by slow evaporation its solution affords prismatic crystals, which are not changed by exposure to the air. It is fused into a glass by heat, and is decomposed by lime, barytes, and magnesia.

Borate of Soda, or Borax of Commerce, is a salt much better known, it having been in use in the arts, and long known to chemists. Homberg first obtained its acid from it, and Geoffroy discovered that it contained soda. It is a native production, being obtained from a lake in Thibet, from the sides of which it is dug up, and where there appears to be a constant reproduction of it. As a natural saline product, it is to be afterwards noticed. In the state in which it is imported, it is impure, from the presence of unctuous matter. It used to be purified by the Dutch by a process kept a secret. Pelletier has shewn that the unctuous matter may be destroyed by calcination, and that then the salt may be obtained pure by solution and crystallization *. In the state in which it is met with in the shops, it is in the form of crystalline masses, of a figure irregular, but approaching to an hexaedral prism.

The borax of commerce is not a perfectly neutral salt; it always contains an excess of soda, which seems necessary to cause it to crystallize; hence it changes the vegetable colours to a green. Its taste is cool, and somewhat alkaline; it is soluble in 12 parts of cold, and in 6 parts of boiling water; it is very slightly efflorescent.

This salt when exposed to a moderate heat, melts from the water of crystallization it contains. When that is evaporated, there remains a dry spongy white mass, which is termed Calcined Borax. If the heat be raised to ignition, this is easily melted into a pellucid glass which suf-

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* Memoires de Chimie, t. i. p. 82.

fers no decomposition, as it can be redissolved in water, and crystallized.

Borax is decomposed by the greater number of the acids and by potassa and the earths, the former uniting with its alkali, the latter with its acid. According to Bergman it consists of 34 parts of boracic acid, 17 of soda, and 49 of water. As I have already observed, it contains an excess of alkali, or is a sub-borate of soda. The properties of the perfect neutral salt are little known. It may be prepared by adding the necessary quantity of boracic acid to a solution of borax; this solution cannot be crystallized, but forms by evaporation a gelatinous mass. It is not at all used.

Borax fused with the more refractory earths, silex and argil, combines with them; and if there be a considerable excess of borax, the compound is soluble in acids; hence its use in mineral analysis.

From this facility with which it melts and brings other substances into fusion, it is of use in some arts, as in making of glass, especially the finer glass for imitating the gems, in assaying minerals by the blowpipe or by heat applied in a crucible, and in soldering the more valuable metals, the borax melting, and covering the bright surfaces of the metals to be joined, so as to prevent their oxidizement by the necessary degree of heat, and exposure to the air.

Borate of Ammonia.—This salt is little known, and can scarcely indeed be obtained in a solid state. If ammonia is saturated with boracic acid, on evaporating the solution, the greater part of the ammonia is disengaged. Some chemists, however, have obtained from this combination prismatic crystals, of a sharp taste, and which change the vegetable colours to a green. These have evidently an excess of alkali: by heat they are entirely decomposed, the ammonia being expelled.

Borate of Barytes.—Borate of Barytes is formed by adding Boracic acid to barytic water: it is precipitated in the form of a white powder, insipid, and insoluble.

Borate of Strontites.—Boracic acid, added to a solution of strontites in water, forms as it is neutralized a copious precipitate. This borate, which appears to have a tendency to form with an excess of base, requires about 130 parts of boiling water for its solution, and is scarcely acted on by cold water.

Borate of Lime.—When this salt is formed, by adding a solution of borate of soda to lime-water, or to the solution of any of the soluble salts of lime, it is precipitated in the state of an insoluble powder, white and insipid, the properties of which have not been more particularly examined.

Borate of Magnesia is little known. The earth is dissolved by the liquid boracic acid, and the solution, on evaporation, affords a crystalline matter, of no regular form. It is also formed by adding the solution of any of the alkaline borates to any of the soluble magnesian salts; the borate of magnesia being precipitated in the state of an insoluble and insipid precipitate.

The compound of boracic acid with magnesia and lime, and with minute quantities of silex, argil, and oxide of iron, exists in nature. It was formerly named Cubic Quartz, now Boracite. It occurs crystallized, in cubes, which are so hard as to scratch glass; semi-transparent; of a white colour; with a shining lustre. They become electric by heat; fuse before the flame of the blowpipe, with ebullition; and form a yellow enamel. It does not effloresce, or dissolve in acids, unless heat be applied. It is found near Luneburg in Hanover. It consists, according to Westrumb's analysis, of boracic acid 68, magnesia 13.5, lime 11, silex 2, argil 1, oxide of iron 0.7.

Borate of Argil.—When argillaceous earth, newly precipitated from any of its soluble salts, is digested with boracic acid, there is deposited, by continuing the evaporation, a viscid substance, through which minute crystals are interspersed, having a very astringent taste, and which is probably borate of argil.

Boracic acid acts very feebly on the metals. It is scarcely able to dissolve any of them, but it may be combined with their oxides by a complex affinity. The mode of effecting this is to mix a solution of the metal in nitric acid, with a solution of borax, when the boracic acid unites with the metallic oxide,—the nitric acid combining with the soda. These combinations are afterwards to be described.

NOTES.

NOTE D. *(p. 52.)*

I HAVE stated in the text the theory of the constitution of the atmosphere proposed by Mr Dalton, and have given a sketch of the one that may be opposed to it, founded on the principle, that between the particles of mixed gases, chemical attraction may be so far exerted as to prevent their separation, or counteract the difference in their specific gravities, without bringing them into intimate union. This principle, I have observed, derives much support from the views of chemical affinity suggested by the speculations of Berthollet, and he himself has applied it to this subject *. I have now to state briefly the arguments which appear to establish this doctrine, and which may be urged against the theory of Dalton.

What appears to be the principal error in the reasoning by which Mr Dalton endeavours to support his hypothesis, is the assumption, implied at least, if not directly expressed, that if chemical attraction be exerted between the particles of bodies, it must always cause their intimate combination, and form a substance possessed of new properties ; and that where such a combination does not happen, we have no reason to infer the existence or the exertion of any attraction. Now this assumption does not appear to me to follow from any just view of chemical affinity, but precisely the reverse, and it will be found inconsistent with a number of chemical facts.

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* Chemical Statics, vol. i. p. 332.

In considering the cause of chemical combination, we are not to view it as arising merely from the exertion of one force: several powers have almost always operated before it has been effected, and its accomplishment is owing to the predominance of one power over others which have opposed it. In the solution of a solid, for example, there are exerted, the force of affinity between the solid substance and the solvent tending to unite them, and the cohesion of the solid tending to retain its particles in aggregation, and to prevent their union with the particles of the fluid. If the former predominate over the latter, the solution takes place; if, on the contrary, the latter be more powerful, no solution happens. But, even in this latter case, it cannot be doubted but that the affinity of the liquid to the solid had been exerted: it only was insufficient to overcome the antagonist powers; and therefore the combination was not effected. The proof of this is, that if the latter power be overcome by other means, the exertion of the attraction will be successful, and the combination will take place. Take the example of potassa and silex. If we pour a solution of potassa on a piece of quartz, the quartz, or its silex, will not be dissolved. But if we precipitate silex from the *liquor silicum*, in which case we have it in a state of comparatively weak aggregation, and add to it the same solution of potassa, a perfect solution will speedily be effected. Now it can surely not be doubted, but that the potassa, when poured on the quartz, exerted an attraction to the particles at its surface tending to combine with them, but that this attraction was not sufficiently strong to overcome the cohesion, and detach the particles to unite with them. The diminishing the cohesion in the second experiment, could obviously add nothing to the force of affinity, or *cause* it to be exerted: it only removed an obstacle to its effective exertion, and hence produced the combination. We see, therefore, in this example, that an affinity has existed, and must have been exerted, where a combination did not take place; of course, that from intimate combination not happening between two bodies, we are not to infer the absence of all attraction, or conclude that they are indifferent with regard to each other. Numerous similar examples, as the action of acids on the sapphire, and other varieties of argil in a state of great aggregation, might be stated.

The same conclusion is to be drawn from the effect of temperature on solution. If a fluid is poured on a solid, and does not dissolve it unless the temperature be raised, it is not to be inferred, that the increase of temperature *caused* an attraction to be exerted between them: the attraction which effects the solution must always have been exerted, and the rise of temperature favours the solution, by diminishing the force which opposed that attraction,—the aggregation of the solid substance. This proves to us, therefore, that attraction is not exerted merely when it is effective, but before this, and that its being effective is owing rather to the powers acting against it being overcome.

If we consider the attractions exerted between the gases, we shall find the same reasoning equally applicable, and the same conclusion as clearly established. The results of their mutual actions we are not to consider as arising merely from the attractions exerted between them, but as modified by the elasticity in each, which acts as an antagonist power. When two gases, therefore, combine intimately, we are not to ascribe the combination simply to the affinity exerted between them, but to the preponderance of this affinity over the elasticity which opposed their union; and, on the other hand, when two gases presented to each other do not unite, this is not to be regarded as a proof that they have no attraction to each other, or that this attraction was not exerted, but that it was not exerted with sufficient force to overcome their elasticities. The same train of reasoning which leads to the conclusion, that when a solid and liquid, known to have mutual affinities, have not united, still their mutual attraction had been exerted with a certain force, equally leads to the conclusion, that when two gases, known to have an affinity, or, in other words, known to be susceptible, under certain circumstances, of combination, have not united when presented to each other, they have still exerted that attraction, though, from the predominance of the opposing circumstances, it has not become effective ; *and we arrive at the conclusion, that between mixed gases, which are capable, under any circumstances, of combining, an attraction must always be exerted with at least some degree of force, should even those circumstances, which are necessary to their intimate union, not be present, and, of course, that union not take place.*

The general nature of this weak reciprocal action of gases, is well stated by Berthollet in the following paragraph ; it being necessary to recollect, that he employs the term combination to denote that case of chemical union which is intimate, and attended with change of constitution and properties, and solution to express that where the substances are united without condensation or material change. "When different gases are mixed, whose action is confined to this solution, no change is observed in the temperature, or in the volume resulting from the mixture ; hence it may be concluded, that this mutual action of two gases does not produce any condensation, and that it cannot surmount the effort of the elasticity or the affinity for caloric, so that the properties of each gas are not sensibly changed, while in the mutual solutions of liquids a condensation takes place, and in that of solids there is frequently observed a dilatation accompanied by a production of cold, which is owing to the reciprocal affinity opposed to the combination with caloric being diminished : thus although both the solution and combination of two gases are the effect of a chemical action which only differs in its intensity, a real difference may be established between them, because there is a very material difference between the results : the combination of two gases always leads to a condensation of their volume, and gives rise to new properties ; in their solution the gases share in common the changes arising from compression and temperature, and preserve their individual properties, which are only diminished in the ratio of the slight action which holds them united *."

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* Chemical Statics, vol. i. p. 198.

We accordingly find, that from the different degrees of energy with which these forces are exerted, numerous shades of combination, and some of them accompanied by no change of properties, and scarcely by any condensation, are effected. In the solutions of salts in water, the attraction exerted is merely sufficient to give fluidity to the solid, and to counteract its cohesion and specific gravity; the properties are not altered, and, in many cases, so little is the condensation, that the enlargement of volume from the liquefaction counteracts it, and the density is near that of the mean density, or is even sometimes less; and in the solutions of various vegetable principles, in water or alkohol, even change of density is not perceived. May it not be concluded, that such weak attractions may be exerted between aëriform bodies,—attractions sufficient to counteract their elasticity, and difference of specific gravity, without being sufficiently energetic, at certain temperatures at least, to cause an intimate combination, so that the two particles of the respective gases should form one?

This principle may be applied to the explanation of the constitution of the atmosphere, and the application is sufficiently obvious. It has appeared as a fair deduction from the phenomena of chemical affinity, that an attraction may be exerted between two substances, though it may not be sufficient to overcome opposing forces, so as to unite them intimately; and the farther assumption will not surely be regarded as an improbable one, that this attraction may counteract the difference in the specific gravities of these substances, especially where it is not considerable, and prevent them from separating from each other. If it be admitted, it accounts satisfactorily for all the phenomena, or it reconciles the only two facts which, on former hypotheses, appeared incompatible,—the uniformity of the composition of atmospheric air, and it having no properties different from those of the oxygen and nitrogen, of which it is composed. Nor perhaps does it require any particular observation to prove, that the principle of this theory is more just than the one Mr Dalton has proposed. Although the assumption, that mixed gases neither attract nor repel each other, may afford an explanation of the constitution of the atmosphere, it is not attempted to be established by any species of proof, or rendered probable by any reasoning. And it must surely be regarded in the abstract as improbable. The repulsion between the particles of any individual gas, is owing to the operation of caloric, and is a necessary attribute of the form in which it exists; and why should there not be the same repulsion between the particles of two bodies in this form? What cause can counteract it, but a chemical attraction exerted between them? The one power may balance the other, and may produce that state of indifference which Mr Dalton has supposed to exist, without assigning any cause by which it could be produced; or, rather, it may give rise to that slight state of combination, of which there are examples in chemistry, where there is little or no condensation, or change of properties, and where the particles seem not to be united together, so as to form one substance.

Nor is the principle unsupported only; it is in itself improbable, and may be deemed inconsistent with the truths that have been established respecting the exertion of chemical affinity; for it appears extremely probable, that all the varieties of matter are capable of exerting reciprocal attractions, and that these are only prevented in particular cases from being apparent by foreign or external circumstances, though they still exist, and operate even with a certain force. The state of elasticity, though unfavourable to combination, is not necessarily incompatible with the exertion of chemical attraction; for there are a number of gases which combine when presented to each other. It is true, that these in general require a high temperature; but this does not alter the state of the fact; and there are others in which even this is not requisite. The difference of temperature too, even in the former, is so inconsiderable, when compared with the whole range of temperature, that it does not lessen the probability of a conclusion, suggested by the most correct views of chemical affinity,—that if at one temperature the particles of gases attract each other, they may do so with a certain force at another; that if oxygen and nitrogen can exert a mutual attraction at a red heat, as we know they do, they may exert the same attraction at lower temperatures with diminished force.

From these observations I trust it will appear, that a theory of the constitution of the atmosphere different from Mr Dalton's may be delivered, equally satisfactory in accounting for the phenomena to which it relates, and that this theory is more probable in its first principle, and founded on juster views of the action of chemical affinity. Mr Dalton's ingenious theory may perhaps satisfy the mechanical philosopher, but it will scarcely be regarded by the chemist as consonant to the general train of chemical facts.

(*p.* 57.)—CONNECTED with the theory of the constitution of the atmosphere, as to the nature of the relation between the permanent gases, is the consideration of the state in which the watery vapour it contains exists,—whether it is chemically combined, or mechanically diffused. The conclusion formed with regard to the one, will probably be extended to the other, though there may be some arguments in some measure restricted to each. As thus connected, I have placed, at the end of this note, the consideration of the questions, To what is the elevation of water in vapour in the atmosphere to be ascribed, and in what state does this vapour exist in atmospheric air?

I have stated in the text, that three theories have been maintained on this subject. The one of oldest date is that which was suggested by Dr Halley, and afterwards maintained and illustrated by Le Roy, Hamilton, and Franklin. It ascribes spontaneous evaporation to a chemical attraction exerted by the air to the water, and is compared by Halley himself to the solution of a salt in water; the air dissolving the water as water does a salt, the solvent power in both cases being increased by heat, and the matter dissolved being separated or precipitated when the temperature is reduced. Other analogies were pointed out in favour of the theory; such as the acceleration of evaporation by a current of air, this renewing the solvent, and of course preventing that approach to saturation which would take place in quiescent air, and which, in conformity to the usual law of chemical attraction, would impede the solution. The increase of evaporation, in a given quantity of water, by enlarging its surface, was explained on the same principle, as it is thus more freely acted on by being more exposed to the attraction of the solvent. And, lastly, in support of the principle of this theory, it was observed, that a chemical affinity did exist between air and water, since not only is the latter combined with the former, but a portion of air is likewise combined in water, and retained by a considerable force.

According to this hypothesis, as it may now be stated, water passes into vapour at common temperatures, and under a common atmospheric pressure, in consequence of the attraction exerted towards it by atmospheric air, or the gases composing it: "it acquires from the elastic state thus procured to it, exactly the same properties as it has when reduced into vapour by the action of heat, or the action of the air consists in maintaining the water in an elastic state, and in communicating to it the properties of a permanent gas, as far as the term of saturation *."

One fact, however, which was observed, led to an opposite theory. Water, even at the common temperature of the atmosphere, was found to pass into vapour *in vacuo*. Thus, in the vacuum of the air pump, it evaporates very perceptibly at 70° of Fahrenheit; and Mr Watt shewed, that at still lower temperatures, and in the more perfect Torricellian vacuum, the same evaporation takes place. A drop of water was admitted into the column of mercury in the barometer at the temperature of 57°. On rising to the surface of the quicksilver, it began to evaporate, and the vapour by its elasticity depressed the mercury half an inch. Since it is proved, therefore, that water passes into vapour *in vacuo*, or without the agency of atmospheric air, it was concluded, that its spontaneous evaporation, under exposure to the atmosphere, is not owing to that agency, but merely to the agency of caloric. Two modifications of this opinion were proposed. By Saussure, the vapour, after it was formed and mingled with the atmosphere, was supposed to be chemically combined with it. By De Luc, it was supposed still to exist in the state of vapour uncombined, and merely intimately mixed or diffused. In conformity to his views of the constitution of the atmosphere, Mr Dalton adopts the latter hypothesis. Water, at every temperature, he considers as convertible into vapour by the sole operation of caloric: the vapour thus formed exists in the atmosphere in a distinct state, neither attracted nor repelled by the other gases, but supporting itself by its own elasticity, the quantity of it present being dependent on the temperature, and the amount of the pressure exerted by the quantity of vapour already formed.

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* Chemical Statics, vol. i. p. 211.

If the discussion were confined to the two modifications of the opinion, which equally assume that the conversion of water into vapour arises merely from the operation of caloric, the views which have been already suggested on the constitution of the atmosphere, would lead to the adoption of the hypothesis of Saussure, that the vapour is in a state of combination, not intimate perhaps, but such as must be produced by some attraction exerted towards it by the permanent gases. The same reasoning which leads to the conclusion, that an attraction, however weak, must be exerted between these gases themselves, the oxygen, nitrogen, and carbonic acid in the atmosphere, equally leads to the conclusion, that an attraction must be exerted between each of them and the watery vapour; and those who admit the one opinion must maintain the other.

But I conceive we may go farther, and, without any particular reference to that conclusion, or the reasoning on which it rests, be able to render it probable, that the conversion of water into vapour is not owing to the operation of caloric alone, but is influenced by the affinity of air to water; that, therefore, the original theory of spontaneous evaporation is the most just.

It has always appeared to me, that there is a striking fallacy in the conclusion, that because water passes into vapour *in* *vacuo*, at a natural temperature, it will pass into vapour at least to the same extent, at the same temperature, under a common atmospheric pressure. The pressure of the atmosphere diminishes or prevents the evaporation of other fluids. Why should it not have the same effect on water? and if it have, what proof is there that water under that pressure will pass into vapour, independent of the agency of the air? The conclusion is indeed extremely illogical. It is acknowledged, that atmospheric pressure alters the boiling points of fluids, or that it has a powerful effect in preventing the transition of substances into the elastic form. By placing water *in vacuo*, the chemical agency of the atmosphere is indeed removed, but its mechanical pressure is also removed; and nothing can be more gratuitous than the conclusion, that because it passes into vapour under the absence of this pressure, it will equally do so when subjected to it. The proper manner of making the experiment is to exclude the chemical agency of the air, while the pressure of it is preserved;—in other words, let water be placed *in vacuo*, under the pressure of a column of mercury 29 inches in height, which is equal to the pressure of the atmosphere. If in this case any vapour were formed, the conclusion would be just, that spontaneous evaporation is independent of any chemical agency of atmospheric air. But the fact will be found very different; for, although water introduced into the tube of the barometer at 60°, passes into vapour, and depresses the mercury half an inch, that vapour will be completely condensed, and the water retained in the fluid form by a pressure a little greater, instead of being able to exist under the pressure which is equal to that of a column of mercury 29 inches high.

It is to be observed, however, that the force of this reasoning is so far eluded by a position maintained in Mr Dalton's reasoning, that pressure does not prevent the evaporation of liquids,—a position which appears to follow indeed from his hypothesis, that mixed gases do not repel each other; for suppose vapour to be formed from water, at a natural temperature, and to be diffused through the atmosphere, as it is neither attracted nor repelled by the contiguous gases, it will not be subjected to their pressure, and hence it will exist to the quantity which can be formed at that temperature independent of that pressure. Were, therefore, says Mr Dalton, every part of the atmosphere except the aqueous vapour instantly annihilated, little addition would be made to this aqueous atmosphere, because it already exists in every place almost entirely up to what the temperature will admit.

This may be granted, yet still the difficulty is merely eluded, not fairly met. If water were converted into vapour, it would not, according to Mr Dalton's views, be condensed, since the gases composing the atmosphere are supposed to have no action on this vapour. It may even be admitted, as Mr Dalton states, that the quantity of vapour formed, suppose the pressure of the atmosphere to be removed, would not be much greater than what at present exists in it; for that vapour would itself form an atmosphere, which, at a given temperature, can exist only to a certain extent, and which by its pressure would prevent the farther transition into vapour, But the difficulty in the hypothesis, is not how the vapour, were it formed, can exist uncondensed; but how the transition of the water into vapour can be effected; and it still appears to me that this affords a demonstration of its fallacy. Elastic fluids press on the surface of liquids. This the barometer, syphon, and innumerable facts, demonstrate. The pressure exerted by the atmosphere is equal to that of a column of quicksilver 29½ inches in height. Place water under the pressure of such a column, and indeed under one much less, none of it passes into vapour. How, therefore, if we exclude the agency of the affinity exerted to it, should it pass into vapour under the pressure of the atmosphere? The exertion of that pressure on the surface of the water cannot be denied; and can it be conceived, that some particles should be exempted from it, and be allowed to escape, while the entire surface is exposed to it? Yet to this strange supposition Mr Dalton is obliged to have recourse. He supposes, "that it is not till the depth of 10 or 12 strata of particles of any liquid, that the pressure upon each perpendicular column becomes uniform; and that several of the particles in the uppermost stratum are in reality subject to but little pressure *." The improbability of such a supposition is evident; and it is not less so that it is an accommodation to the hypothesis.

Mr Dalton has also said, that the difficulty is the same on the opposite hypothesis. I rather think that it is not, and that indeed on this hypothesis it is easily accounted for; for another power is introduced, the affinity of the atmospheric gases, which may overcome the pressure, and elevate a portion of the water in vapour: and the quantity elevated, it is to be remarked, is comparatively small. This affinity, Mr Dalton adds, is described as weak; and he presumes, therefore, that it is inadequate to this effect; but it is weak only when considered in relation to the opposing circumstances,—the elasticity of the gases of the atmosphere when they are to be absorbed by it, and the elasticity of the vapour when, in consequence of its exertion, water has passed into that form.

It appears to me, therefore, that the theory is still liable to the original objection, that of resting on the conclusion not only illogical, but inconsistent with fact,—that if water pass at a certain temperature into vapour *in vacuo*, it will equally pass into vapour at the same temperature under the atmospheric pressure, independent of any attraction exerted to it by the air.

Independent of this position, on which the theory primarily rests, a fact has been alleged and strongly urged in its support. It is, that at a given temperature the quantity of watery vapour contained in any gas is the same as that contained in any other. This was established by Saussure with regard to common air, carbonic acid gas, and hydrogen gas, at least he found that these gases, under similar circumstances, came to the same hygrometrical state †. It has since been confirmed by the experiments of Clement and Desormes, and extended to all the gases; the same quantity of water, according to these chemists, being taken up by all of them under the same circumstances ‡. Now, if the conversion of water into vapour were owing to the operation of caloric alone, and if the vapour, after it is formed, were merely mechanically mixed with the gas, this is what might be expected; but if its conversion into vapour were owing to an affinity exerted by the gas towards it, it must appear improbable that the affinity should in all of them be of the same force; it rather follows, that the different gases would exert attractions differing in force, and that therefore water, in contact with them, would be dissolved in unequal quantities, or in larger proportions by some than by others.

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* New System of Chemical Philosophy, p. 193.

† Essais sur l'Hygrometrie, p. 231.

‡ Annales de Chimie, tom. xliii. p. 125.

Nay, the argument may be placed under a still stronger point of view; for it is affirmed, that the quantity of watery vapour in any gas is the same as that which would be contained in a vacuum of the same space as that which the gas occupies. This too was ascertained by Saussure, and has been established by De Luc and Dalton; which appears to prove, that the gases exert no affinity which causes the evaporation, or at least no affinity to the vapour formed, since if they did, this law would not be observed. It cannot be conceived, it may be said, that the affinity of the gases to water should in all of them be of the same force, and that force proportioned too, not to the quantity of matter, but to the space they occupy; and the inference appears just, that the transition of the water into vapour, and its existence in that state, is independent of any chemical action of the gases, or in spontaneous evaporation of any chemical agency of the atmospheric air.

But it is not clear that the fact is established. Setting aside the experiments of Saussure, which he himself does not regard as proving that the same quantities of water are present in different airs indicated by his hygrometer to be in the same hygrometrical state, (for he very properly distinguishes between the saturation of airs with humidity, and the quantities requisite to produce that saturation), what proof is given of its truth? The principal one is derived from its being found, that the elasticity exerted by watery vapour in different airs at the same temperature is the same. A quantity of water is allowed to pass into vapour *in vacuo*, and its elasticity measured by the depression it occasions in a column of mercury; this at 65°

being such as to cause a depression of 0.5 inch : a quantity of dry air is put into a vessel of the same capacity as the vacuum, and a little water introduced, the temperature being the same; it passes into vapour, and the acquired elasticity is found to be the same as that in the vacuum, or at 65° will cause a rise in an included barometer of 0.5 inch ; and if any other gas be substituted for atmospheric air, the result is still the same. Hence it is concluded, that the same quantity of water has in all these cases been converted into vapour.

But it is a just observation of Mr Gough on this conclusion, that the elasticity exerted by vapour under these different circumstances, is not a measure of its quantity, unless it be taken for granted, what of course is the point in dispute, that that vapour is uncombined. If the vapour be in a state of combination with the gases, this will restrain and limit its elasticity ; and the more powerful the attraction exerted, the diminution will be greater ; and hence it may happen, that at the point of saturation, or where the affinity is balanced by the elasticity, the same elastic force will be exerted in all these cases, though the quantities present may be different, and their force may be the same with that exerted by uncombined vapour at that temperature.

To develope this observation a little farther.—In supporting the theory that spontaneous evaporation arises from an attraction exerted by the air to water, it is conceived, that in consequence of that attraction the water passes into vapour, and that this vapour combines with the air, or rather with the gases composing it, the combination not being of the intimate or energetic kind. Now, what will place limits to this combination? Undoubtedly the elasticity of the watery vapour. The two powers are antagonists : the combination will proceed until the elasticity is at its maximum, and the attraction become very nearly a negative force ; and in this state the elasticity will be the same in all of them, and the same, or very nearly so with that of watery vapour in an uncombined state. Hence the law which has been experimentally proved, seems to follow as necessarily from this theory, as from the hypothesis that the watery vapour contained in a gas is in an uncombined state.

It has been attempted to be shown by another kind of experiment, that the quantities of water contained at the same temperature, and under the same pressure, in the different gases, are the same. When exposed to the action of substances which have a strong attraction to water, they deposite, it is said, from equal volumes, the same quantity of humidity. This appears to be established by the experiments of Clement and Desormes. They exposed several gases, saturated with moisture, successively to the action of muriate of lime, a substance which has a very strong attraction to water, and observed the quantity deposited by the increase of weight in the muriate of lime. The following table gives the results *.

Gases desiccated.	Water deposited by 36 Litres.	Water which would be deposited by a Cubic Foot.	
	Grammes.	Grammes.	Grains.
Atmospheric Air	0.33	0.313	5.89
Oxygen Gas	0.34	0.323	6.08
Hydrogen	0.34	0.323	6.08
Nitrogen	0.33	0.313	5.89
Carbonic Acid	0.33	0.313	5.89

Although, however, in these experiments, the same quantities of water were deposited from the different gases, or at least with differences so inconsiderable, as might arise from the unavoidable imperfection of the process, Clement and Desormes are themselves aware, that this is no conclusive proof that these gases, under the same circumstances, contain the same quantity; for they observe, that it still " remained to know, whether the quantities of water which cannot be taken from water by desiccation, are equal ;" and they admit, that " it was almost impossible to ascertain this point by a direct experiment ;" nor indeed did they draw any conclusion but from analogy. It is sufficiently evident, that by such experiments, the question remains undetermined. The very difference in the strength of

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* Philosophical Magazine, vol. xiii. p. 69.

affinity, which may give rise to some difference in the quantity contained, will oppose proportionally an obstacle to any method by which it is to be abstracted. As one gas will contain more water than another, only from exerting to it a stronger attraction; so this superior attraction will enable it to retain a larger quantity when exposed to the action of substances having a tendency to abstract it; and thus the different gases may deposite the same quantities, but still retain different quantities.

It is also to be observed, that the differences in the quantity of watery vapour in the different gases is probably not considerable; perhaps even scarcely appreciable. This is owing to the little energy of the action exerted by the gases on the vapour, from the mutual elasticity. By their attraction to water, they convert it into vapour; but, while the attraction is thus satisfied, the acquired elasticity renders the combination of the vapour with the gas comparatively weak. Hence, as the elasticity is in all cases the same at the same temperature, as it acts with so much force in counteracting the affinity, and as differences in the forces of their affinities exerted by the different gases are inconsiderable, it must follow, that the difference in the portion of water dissolved will be inconsiderable, and scarcely if at all capable of being estimated.

That the gases do differ in the force of their affinities to water, while the difference is at the same time inconsiderable, is apparent from the fact, that quantities unequal, but not greatly so, are absorbed by water under the same pressure; 100 cubic inches of water taking up, for example, 3.5 of oxygen, 1.4 of nitrogen, and 1.5 of hydrogen. Were it granted that such differences do not exist in the quantities of water dissolved in these gases, (though that they do not remains to be ascertained by experiment), this must be owing partly to the small quantities of matter acting in a given volume, and partly to the difference being limited by the resulting elasticity, as just now explained.

The conclusion I believe, therefore, may be drawn, that these facts are not subversive of the opinion, that spontaneous evaporation is owing to an affinity exerted between air and water.

Though I believe it has been shewn, that the hypothesis, which considers spontaneous evaporation as owing to the agency of caloric alone, rests on a principle not justly inferred, and involves conclusions inconsistent even with familiar facts, some proof may be demanded of the truth of the opposite doctrine. Such proof, I conceive, may be given, and facts stated in favour of it, irreconcileable with any other.

I shall draw no argument in its favour from the analogies between evaporation and other varieties of solution, as, although they accord with the theory, they also admit of explanation on the other.

Some weight, however, must be given to the general argument from the nature of chemical affinity,—that it is a force of which we have numerous gradations, but which, in almost all cases, operates to a certain extent. No doubt can be entertained of the attraction between some gases and water, as they are absorbed by it in very large quantity; such are its combinations with ammonia or muriatic acid. And as all attraction is reciprocal, these gases will hold a portion of water in solution, which will be limited by the elasticity of the gas, and the acquired elasticity of the water. Is the probability not apparent, that the same forces will be exerted between water and other gases, only perhaps in weaker intensity? The most correct view perhaps of the nature of chemical affinity, leads to the conclusion, that oxygen, nitrogen, hydrogen, and every body in the aërial form, will exert an attraction to water, though it may be with different degrees of force. This affinity will always be opposed, first by the elasticity of the gas itself, and secondly by the elasticity acquired by the portion of water, which by that affinity may be made to pass into the form of vapour. Limits will thus be placed to its exertion; but it is reasonable to believe, that it will always be exerted to a certain extent.

It may be said, that this reasoning rests on an hypothetical view of the laws of chemical affinity, and can have weight only with those who admit this view. It has, however, all the probability belonging to that theory; and to those who have duly estimated it, this will not be deemed inconsiderable. But, independent of this, other arguments more direct may be stated.

We find, that a chemical attraction does exist between water and the gases composing atmospheric air. This is proved by the fact, that water absorbs those gases, and retains them with considerable force, in a state of solution. Since all attraction is mutual, atmospheric air must be equally capable of dissolving water in a quantity regulated by this affinity, and by the existing and resulting elasticity.

Mr Dalton conceives indeed, that the relation between these gases, as well as others which are not absorbed in greater quantity, and water, is merely mechanical; the quantity of gas that does appear to be absorbed being merely forced, as it were, into the pores of the water by pressure; and this appears to be confirmed by the discovery by Mr Henry of the law which regulates this absorption,—that at a given temperature the quantity absorbed is precisely proportioned to the pressure applied, or, " under equal circumstances of temperature, water takes up, in all cases, the same volume of condensed gas, as of gas under ordinary pressure." But, admitting this law, of which the well-known accuracy of Mr Henry leaves no room to doubt, it does not appear to me, as I have already remarked, (p. 144.), that the conclusion follows which has been drawn from it. In the absorption of gases by water, two powers operate, or may be conceived to operate, independent of pressure,—the affinity between the gas and water tending to combine them, and the elasticity of the gas counteracting this, and placing limits to the combination, precisely in the same manner as in the solution of a solid, there are two forces operating, the chemical affinity, and the cohesion of the solid. In the absorption of a gas, whatever favours the exertion of the elasticity will lessen the quantity absorbed; whatever represses it, will promote the absorption. These effects are produced by variations of mechanical pressure; the diminution of pressure favouring the exertion of elasticity, and *vice versa*. But from this no just argument can be drawn against the conclusion, that a chemical affinity exists, and is the primary cause of the combination; and the law stated by Dr Henry agrees as well with the one theory as with the other.

Precisely the same effects arise from temperature. If the temperature of the fluid be high, the absorption of the gas is counteracted, or if it has been previously effected, it is expelled, and that although the pressure remain the same.

That the gases have a chemical affinity to water, is undeniable with regard to some of them, as muriatic acid, fluoric acid, or ammonia; and from those which are absorbed with rapidity, and in large quantities, there is a gradation in extent of absorption to others, which leads to the conclusion, that in all it is owing to the same power. And what at once establishes this view, and confirms the justness of the above reasoning, is, that the absorption of those gases in which the operation of affinity is not denied, of muriatic acid gas for example, is increased by pressure like that of the others, and, I have no doubt, according to the same law. Another fact, equally irreconcileable to the hypothesis, that the absorption is owing to mere pressure, is, that the quantities of the gases which are supposed to have no affinity to water, absorbed under the same pressure, is different. Thus water exposed to atmospheric air absorbs oxygen in preference to nitrogen, and absorbs it in larger quantity, though the pressure of the column of oxygen in the atmosphere is, according to Mr Dalton, equal only to that of 7.8 inches of mercury, while that of nitrogen is equal to 21.2. To what can this be ascribed, but to the different affinities of these gases to water? In the same way, under a given pressure, a much larger quantity of carbonic acid gas is absorbed, than of these gases, equally proving the influence of elective affinity in determining the absorption.

The fact, likewise made the subject of accurate experiment by Mr Henry, that a gas is retained in water more effectually by the pressure of a quantity of the same gas than by that of another, is to be explained partly from the affinity of the one gas to the other, which assists the separation, and partly from the affinity of the second gas to water, which tends to dislodge the first.

I consider it therefore as sufficient proof of the existence of a chemical attraction between the gases in the atmosphere and water, that they are absorbed by that fluid; of course this affinity must be exerted, and equally promote the solution of water by these gases.

Scarcely any objection has been made to this theory of any force, or no fact is brought forward for which it does not account. It has been said, that were it true that evaporation depends on a chemical affinity exerted by air to water, it ought to be more rapid and copious in a dense than in a rare atmosphere, as a greater quantity of the solvent is presented to it, while the reverse is the fact. But this circumstance, no doubt favourable in itself to the solution, is counterbalanced by the increase of pressure, which counteracts, by its mechanical effect, the transition of water into vapour.

It has been stated by De Luc, and given indeed as the reason of his adopting the hypothesis, that spontaneous evaporation is owing merely to the operation of caloric; that the water, in evaporating, absorbs caloric, and renders it latent, precisely as it does when converted into vapour by heat. The futility of this argument is obvious. It does not follow, that the transition of water into vapour, in consequence of a chemical affinity, and the loose combination of that vapour with air, should not be attended with an augmentation of capacity, the same as that which it suffers when it pases into vapour from the action of caloric. This case is precisely similar to the liquefaction of ice by a diluted acid, where the liquefaction is owing to the affinity exerted by the acid, and where the enlargement of capacity takes place, as it does when ice is liquefied by raising its temperature.

A question, scarcely less difficult than what has now been discussed, is that which relates to the cause of the deposition of water from the atmosphere. That it should be deposited as the temperature is reduced, is what might be expected, and accounted for on every theory; but we do not observe that intimate connection which we would look for between these two events, and no very satisfactory theory has been delivered of that rapid and copious deposition which constitutes Rain.

The theory of Dr Hutton on this subject, appeared, if its principle were admitted, to afford a tolerably satisfactory explanation. It assumes, that evaporation is owing to the solution of water in air by a chemical process ; and he observes that this solution may proceed in three ratios with regard to temperature ; it may vary in the same ratio with the temperature, so that equal augmentations of temperature in the air may be accompanied with equal augmentations in the quantity of water dissolved ; it may proceed in a greater ratio ; or, lastly, it may be in a less. In the first case, when two portions of air, at different temperatures, are mingled together, no condensation of vapour will take place, because the whole quantity of air is able to retain dissolved the quantities of water which each portion held in solution. If it be in a less ratio, the mixed air will be capable of dissolving even more water if it were present. It is therefore only in the third case, in which the solvent power of the air increases in a higher ratio than the temperature is augmented, that the precipitation of any portion of water will take place. On the supposition of this being the case, it was conceived by Dr Hutton, that the formation of rain might be explained. When two quantities of air, one at a higher, the other at a lower temperature, each saturated with water, are mixed together, as they may be by winds and currents in the atmosphere, the mixed air, from the hypothesis assumed, will be unable to hold dissolved the whole of the water each portion had in solution; hence a precipitation must take place. This if slow will form clouds or mist. If more rapid, and taking place at some height in the atmosphere, the resistance opposed to the descent of the particles of water will favour the exertion of the attraction of cohesion between them, and cause them to unite in drops, producing rain.

The principle, however, on which the theory rests, has received no proof. An analogical one was advanced by Dr Hutton, derived from the fact, that the very law he supposed, that of the progression of solubility in an increasing ratio with regard to temperature, is observed in the solution of certain salts in water. This, however, when properly considered, is adverse to the hypothesis, and affords an example of the false conclusions to which analogy may sometimes lead, when the principle regulating it is not attended to. The solution of a solid in a fluid is owing to the predominance of the affinity over the cohesion of the solid : an increase of temperature diminishes the cohesion progressively : the obstacle is therefore becoming less as the temperature rises, and, as the affinity remains the same, the solution ought to proceed in an increasing ratio. But with regard to evaporation the result must be precisely the reverse. The obstacle to the mutual affinity between air and water, is the elasticity which the water, by passing into vapour, acquires from that combination. By an elevation of temperature, this elasticity is increased. Hence the obstacle to the combination is becoming more powerful as the temperature rises, and the evaporation ought therefore actually to proceed in a decreasing ratio, or the reverse of what Dr Hutton supposed.

It has frequently been supposed, that electricity is a necessary agent both in the formation of aqueous vapour, and the production of rain. It is affirmed, that when it is communicated to water, it promotes its evaporation ; that the vapour and the fluid are in different electric states, and that the precipitation of rain is often connected with alterations of the electrical state of the atmosphere. But the facts on this subject are either inconclusive, or not well ascertained. That electricity promotes evaporation, appears to have been disproved by Van Marum. He placed cups of water and other fluids accurately weighed on an electrical conductor connected with the machine, and similar quantities were placed unconnected and at a distance from it. The former, after having had electricity communicated for half an hour, were not found to have evaporated more than the others *.

A singular phenomenon attends the deposition of humidity from the atmosphere, under the form of hoar frost : it is attended not with the production of heat, as might be expected when

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* Philosophical Magazine, vol. viii.

a body passes from the aëriform to the solid state, but with a great production of cold. This was observed by Mr Wilson, during an intense cold at Glasgow in 1780. Thermometers laid on the surface of the snow always indicated a temperature lower by 10 or 12 degrees than when suspended two or three feet from the ground. There appeared to be at the same time a deposition of hoar frost. If it could be imagined, that the two processes of evaporation from the ice and deposition of hoar frost went on at the same time, and that the former exceeded the latter in effect, it might be accounted for ; but this cannot be supposed ; the phenomenon is the only one that appears at variance with the theory of latent heat *.

NOTE E. (*p.* 157. 569).

A QUESTION of considerable importance with regard to the chemical constitution of the gases, is that relating to the presence of water in them, in a combined state. It is interesting not only in itself, but from its relation to some chemical facts, particularly to the determination of the composition of the carburetted hydrogen gases, and indeed of all the compound elastic fluids.

In all gases a quantity of water is present, derived from the materials yielding them, or from the water through which they are transmitted. This appears to exist in vapour in a state of loose combination, is capable of being discovered by hygrometrical substances, and may be abstracted by exposing the gas to any matter which has a strong attraction to water, as potassa or lime. The question which has been proposed is, Does the gas, after this portion of what, for distinction, may be named Hygrometric Water, has been abstracted, contain another portion in a more intimate state of combination ?

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* Philosophical Transactions, vol. lxx. p. 451. vol. lxxi. p. 386.

There are some phenomena, particularly those produced by the action of the electric spark on various gases, which have been supposed to establish the conclusion in the affirmative. Dr Priestley, Van Marum, and Monge, had observed, a number of years ago, that when the electric spark is taken for some time in carbonic acid gas, there is always an augmentation of volume, and the gas suffers an evident change, so as to be no longer equally absorbed by water. Dr Austin observed, that in subjecting to a similar operation the heavy inflammable air or carburetted hydrogen gas obtained from the decomposition of acetite of potassa by heat, it is permanently dilated to rather more than twice its original volume, and, when exploded with oxygen, required a larger quantity for its saturation than the gas not subjected to the action of the electric spark would have done; facts from which he drew the conclusion, that charcoal or carbon is a compound of hydrogen and nitrogen [*]. Mr Henry examined this subject with his usual accuracy, and shewed that the proportion of carbon originally existing in the gas is not diminished by this operation; the same quantity of carbonic acid being afforded when it is exploded with oxygen, before and after it has been acted on by the electric spark, and, of course, subverted the theory of Austin, which accounted for the enlargement of volume by the supposed conversion of a portion of carbon into hydrogen and nitrogen. Mr Henry's experiments appeared likewise to shew, that the enlargement of volume is owing to the production of hydrogen, derived from the decomposition of water existing in the gas [†]; and this enlargement happens even when the gas has been previously exposed for a week to quicklime, 186 measures being expanded in an experiment made by Mr Henry to 211, by 130 shocks [‡]. A similar result has been obtained from muriatic acid gas, even when dried by exposure to muriate of lime, Mr Henry having found, that 176 measures thus treated, gave 11 measures of hydrogen gas [§]. He hence concluded that 100 cubical inches of muriatic acid gas, after exposure to muriate of lime, still holds in combination 1.4 grain of water.

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[*] Philosophical Transactions, 1790, p. 51.

[†] Ibid. 1800, p. 196.

[‡] Ibid. 1797, p. 401.

[§] Ibid. 1800, p. 191.

Without intending to deny that water is present in these gases to a certain extent, and may contribute to the enlargement of their volume in the experiments above described, I may observe, that the theory of this expansion, at least in the cases of carbonic acid and carburetted hydrogen, is far from being elucidated; and that the facts with regard to it are so uncertain, as to throw considerable doubts on our conclusions, especially as to the quantity of water which the gases may contain.

In the experiments of Austin on the carburetted hydrogen, there are two facts to be accounted for,—the enlargement of volume, and the increase of combustible matter; and this can scarcely be done, but by supposing water, contained in the gas, to have been decomposed by the metal emitting or receiving the electric spark; the metal, at the high temperature which the spark would excite, attracting the oxygen of the water, and evolving the hydrogen, which would both add to the bulk of the gas, and cause it to require more oxygen for its saturation. But Mr Henry, in another experiment, used a gold wire, which it is probable could not attract oxygen from water, and still there was an enlargement of volume. Here, therefore, the decomposition must have been of a different nature, and probably depended on the agency of the electric spark alone on the gas, the high temperature causing part of the carbon and oxygen of this gas (for there is little reason to doubt but that it is an oxy-carburetted hydrogen) to combine and form carbonic acid or carbonic oxide, and evolving a portion of pure hydrogen, by which the dilatation would be occasioned. In this case, however, there could be no addition of combustible matter, as an anonymous writer in Nicholson's Journal has justly observed *, in stating the difficulty which has now been attempted to be solved; and accordingly, it does not appear to have been proved, that in the experiment made in this way there was any such addition, the dilatation only being observed †. Now, if the

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* Vol. ii. 8vo, p. 185. † Phil. Trans. 1797, p. 409.

carburetted hydrogen itself in this way suffers decomposition, it is obvious, that the whole enlargement of volume which takes place when the experiment is made with an oxidable metal, cannot be exclusively referred to the decomposition of water, but may in part be owing to the same cause; and, of course, that from the enlargement of volume we cannot draw any conclusion as to the quantity of water the gas contained. Accordingly, Berthollet has since admitted, that although he had mentioned this gas as one of those that contain water combined, new observations have proved to him, "that the decomposition of water could have only a very small share in the dilatation it experiences *.

There is nearly the same ambiguity or uncertainty with regard to the facts in the experiment of transmitting the electric spark through carbonic acid gas. Thus, in the one performed by the French Chemists, of which Monge gave the explanation †, it is stated, that when iron wires were employed to convey the spark, the iron was oxidated; hence it was imagined it must have attracted the oxygen of the water existing in the gas, and from this would arise an evolution of hydrogen, by which the volume would be enlarged. It was accordingly found by experiment, that the gas submitted to the action of electricity was a mixture of two elastic fluids; the greater part of it consisted of carbonic acid, and the remainder appeared to be an inflammable gas, which detonated with oxygen.

But from the more recent experiments of Saussure it appears, that it is the acid which in such an experiment is decomposed. He transmitted by copper wires the electric spark through carbonic acid gas, and observed augmentation of volume. On examining the inflammable gas which was produced, he found it to be carbonic oxide; as in burning it required only about one-third of its volume of oxygen, afforded no sensible quantity of water, but was entirely converted into carbonic acid. Berthollet has since admitted, that this renders the argument

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* Philosophical Magazine, vol. xiii. p. 278.

† Mém. de l'Acad. des Sciences, 1786.

which he had drawn from the augmentation of volume in carbonic acid by the electric spark, inconclusive as a proof of the presence of water *.

Mr Henry has shewn, that carbonic acid suffers an augmentation of volume, even when the electric spark is taken in it by platina wires, which are not oxidable; and this expansion appeared to be attended with the production of oxygen and of an inflammable gas, as the gas remaining after the unchanged carbonic acid had been removed, exploded by the spark †. But we have here still a difficulty from the nature of this inflammable gas not being ascertained, as it might be either pure hydrogen or carbonic oxide. Either the water supposed to be contained in the carbonic acid gas might be decomposed by the agency of the electric spark, and resolved into its constituent gases; or by the same agency a portion of the carbonic acid might suffer decomposition, one part of it being reduced to the state of carbonic oxide, while the oxygen derived from this would remain mixed with it and the undecomposed carbonic acid. Mr Henry has lately repeated these experiments, and has informed me, that carbonic acid dried by muriate of lime, and submitted to the action of the electric spark from platina wires, is actually decomposed: it is resolved into oxygen and carbonic oxide gases; and after removing the undecomposed acid, the mixture may be inflamed by an electric spark, and reconverted into carbonic acid. In the decomposition of carburetted hydrogen gas dried likewise by muriate of lime, the volume of the gas he finds is doubled by long continued electrization; no carbonic acid is generated, nor any addition of combustible matter, but charcoal is precipitated, and the evolution of the light inflammable air is the cause of the enlarged volume.

Viewed, therefore, in relation to the present question, these experiments do not favour the supposition of combined water in these gases, since the phenomena are not connected with the action of water: a portion of hygrometric water no doubt ex-

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* Chemical Statics, vol. ii. p. 455.

† Philosophical Transactions, 1800, p. 203.

ists in them as well as in other elastic fluids; but when this is abstracted by exposure to substances having a strong attraction to water, there is no reason to conclude that any sensible quantity of combined water remains. Mr Henry found, indeed, in his experiments made with the view of investigating Austin's theory, that when the carburetted hydrogen gas had been freed as much as possible from water, the volume, instead of being doubled as before, was enlarged only one-sixth of the original volume of the gas; and even this, from his recent experiments, may be owing in part at least not to the decomposition of water, but of the compound gas itself.

It appears to me, therefore, that, from the experiments now considered, there is no proof of the presence of unknown quantities of combined water in gases in general, and that all the phenomena, the solution of which requires the admission of the existence of water, may be accounted for from that portion of hygrometric water which every gas contains, and of which, though it may in a great measure, it cannot be entirely deprived; a minute quantity remaining after the action of any hygrometric substance. That such a quantity, not in any state of intimate combination, may remain after this action, is obvious: for, in proportion as the abstraction proceeds, the remaining vapour from its elasticity expands, and may at length attain such a degree of rarity, that the action of the substance attracting it cannot overcome its elasticity. But the portion which thus remains must be minute; and the phenomena do not warrant the conclusions that have been drawn by Berthollet and Cruickshank with regard to the existence of large quantities of water in aërial fluids,—that 100 cubic inches of carbonic acid gas, for example, contain, as Berthollet has supposed, 10 grains of water, or 100 cubic inches of carburetted hydrogen gas contain, as Cruickshank inferred, 8 or 9 grains.

If there is any gas which appears to contain combined water, it is muriatic acid. This may be presumed, not only from its strong affinity to water, but Mr Henry found, not only that it affords hydrogen when acted on by electricity, but that it affords nearly as much when it has been previously exposed to muriate of lime, to abstract its water as much as possible, as when this condition was not present; the increase of volume in the former case being six parts in the hundred of the gas, and in the latter not more than seven. Yet even with regard to this gas, the quantity of combined water is supposed by Mr Henry to be only 1.4 grains in 100 cubic inches. The question is, Is this hygrometric or combined water? Even that which we name hygrometric is combined with the gas by a weak affinity, which however may vary somewhat in its force; and as of all the substances which assume the elastic form, muriatic acid has the strongest attraction to water, it may contain more of it, retain it with more force, and prevent its abstraction by a hygrometric substance. Mr Davy has observed, that from the action of potassium on muriatic acid gas rendered as dry as possible by chemical means, a much larger quantity of water is indicated existing in it, than follows from Dr Henry's experiments. When the potassium was heated in the dry gas, a violent action took place; the muriatic acid gas wholly disappeared; from one-third to one-fourth of its volume of hydrogen was evolved, and muriate of potash was formed: he concludes, that muriatic acid gas must contain at least one-eighth or one-tenth of its weight of water. Fluoric acid gas afforded a much smaller quantity, obviously from its weaker affinity. The very singular facts stated under the history of muriatic acid gas, with regard to the influence of water on its acid powers, indicate that its quantity is even greater, and its agency in the combination is still more important than any that has been ascribed to it; but these facts are perhaps still too obscure to admit of any certain conclusion being drawn.

There is another set of facts adduced by Berthollet in proof of the opinion, that a portion of combined water exists in carbonic acid. Withering observed, that the native carbonate of barytes could not be decomposed by heat, while the artificial carbonate could; a difference which he attributed to the action of water, which, by its affinity to the carbonic acid, promoted the decomposition, and of which the native carbonate was deprived. Priestley, whose theoretical opinions led him to maintain the existence of much water in the gases, appeared to have confirmed this opinion, by passing the vapour of water over the native carbonate, its acid being then expelled. The native carbonates of lime appear to exhibit the same phenomenon; at least some of them afford only a small portion of carbonic acid when exposed to heat in a vessel which exerts no affinity to their principles; and the disengagement of the acid in the process of calcining limestone, Berthollet supposes to be favoured by the watery vapour arising from the burning fuel.

Admitting these facts, there is an obvious reflection, which does not seem to have occurred to those who have considered them.—What proof have we that the effect of the water is to be ascribed to the affinity it may exert to the carbonic acid, and not rather to the affinity it exerts to the barytes or the lime? We know of no great affinity which it has to water; for, under the pressure of the atmosphere, the water can absorb not more than its own bulk of the gas: we know, on the contrary, that these earths have a very strong attraction to water; attract it rapidly, and bring a large quantity of it into a state of intimate combination. If an elastic ingredient is to be detached by the operation of heat from a substance with which it is combined, what can be imagined more likely to promote the disengagement than the presence of another substance, which has less disposition to elasticity, and to which the fixed body has a strong attraction? This is the precise relation of barytes, carbonic acid and water; and it is more likely that water should facilitate the decomposition, by such an operation,—the attraction it exerts to the fixed, than any attraction it exerts to the volatile ingredient.

The fact has been also stated by Berthollet, as ascertained by Pelletier, that the native carbonate of barytes, at least the Siberian variety, is not acted on by acids, so as to give out the carbonic acid, unless these acids are very much diluted, and thereby capable, as he conceives it, of affording water necessary to the constitution of the carbonic acid gas. But there is a degree of obscurity with regard to the operation of a diluted acid in this case. In an acid in the common state, in muriatic or nitric acid, for example, which are the ones that have been generally employed, there is much more water than can be conceived necessary to the constitution of the carbonic acid gas; why, therefore, on this hypothesis, should it require to be still farther diluted? The artificial carbonate also is easily decomposed by these acids in their concentrated state. Now the small quantity of water which it can contain, can make no essential difference; for, were such a quantity to be added to the concentrated acid, there can be little doubt, from the general facts which have been stated by Pelletier, that it would contribute little or nothing to enabling it to act on the native carbonate. The difference, therefore, must be ascribed to some other cause; but, were it to be ascribed to the affinity the water exerts, it might still be supposed, with as much probability, to be owing to the affinity it exerts to the barytes as to that exerted to the carbonic acid; the former being necessary, along with that of the acid used as the solvent, to displace the carbonic acid, and form the new combination.

In the last place, admitting that in all these cases water operates by the affinity it exerts to the carbonic acid, I see no proof but that the effects may be ascribed to the hygrometric water which the gas is allowed to contain. Suppose carbonic acid in a state of dense combination, from which it is displaced partly by the affinity which water exerts towards it; when the decomposition is effected, the carbonic acid assumes the gaseous form, and the water exerting the affinity to it must take the same form. Now it does not appear to me to follow, that that water must remain in a state of intimate combination with the gas. Even although it may have exerted an energetic affinity to it, yet the elastic form counteracting this, the water, after that form is assumed, may be held in only loose combination, or in the state of hygrometric water, and therefore by this portion all the above effects may have been produced.

There is, lastly, with regard to the general question, an argument *à priori*, which appears to me to demonstrate the fallacy of the opinion which some have been disposed to maintain, that water is essential to all gases, and even to the constitution of the elastic form. There is no chemical deduction established by a stricter chain of evidence, than that from the known agency of caloric, it must be capable of establishing, at one temperature or another, a repulsion between the particles of any matter, or of causing it to pass into the elastic state ; and many do pass into it, quicksilver for example, where the presence of water cannot be suspected. Nay, in the transition of water itself to the gaseous form, the change must be ascribed entirely to the action of caloric. Now, why should it be supposed, that in other cases caloric should not have the same power, or by what species of action can water be supposed essential to the formation, or maintenance of the aëriform state ?

Note F. *(p. 287.)*

Few problems more interesting to the chemist can be presented for solution, than that with regard to the proportions of the ingredients of the neutral salts. It is of importance in the theory of the science, as connected with the doctrine of affinities ; and it is of the first utility in practical chemistry, as abridging the labour of analyses, and securing that exemption from discordant results, which would be unavoidable in experiments so delicate, when made by different individuals. I propose in this note to give an account of the methods that have been employed to attain the solution of the problem.

Bergman, and afterwards Wenzel, endeavoured to determine the proportions of neutral salts, by ascertaining what quantities of acid and base were requisite for mutual saturation ; what quantity of solid salt could be obtained by evaporation ; and, lastly, what quantity of water existed in the crystallized salt, by the loss of weight it sustained at a red heat. But their methods, independent of errors from peculiar causes in single experiments, are liable to important general objections. They did not determine with sufficient precision the strength of the acids they employed, or what quantity of real acid was contained in an acid of a certain strength ; they were not sufficiently aware of the loss which many saline solutions sustain during evaporation, from part of the salt being carried off by its volatility, or its affinity to the watery vapour, or from its suffering decomposition ; and they presumed, what is undoubtedly not just, that at a red heat salts will either retain no water of crystallization, or will all retain nearly the same quantity.

Mr Kirwan, in the course of his investigations on the same subject, discovered these sources of error, and endeavoured to obviate them. At the same time, such is the difficulty of the investigation, that he has been under the necessity of repeatedly altering the methods he employed.

The greatest difficulty, as has been remarked, is that of determining the strength of acids ; or, as the acids in the state in which they are presented to us are combined with water, to discover what quantity of real acid they contain. Mr Kirwan at the commencement of his researches supposed, that muriatic acid existing in the state of gas, was in the state of real acid ; and from this, by experiments on the quantities absorbed by water, and the density of the solutions, he inferred the quantity existing in liquid muriatic acid of different specific gravities. He further supposed, that of the other acids, at least of the sulphuric and nitric, the same quantity of real acids would be requisite for the saturation of an alkaline base,—of potassa ; and therefore, by ascertaining what quantity of real muriatic acid (as he supposed it to be) was expended in this saturation, and what quantities of the other acids of certain specific gravity were necessary for the saturation of the same quantity of the same base, he obtained the data whence the quantity of real acid in all of them could be calculated. On these principles his investigations as to the quantities which entered into the composition of the various salts, were founded *. Independent of particular objections, there can be no doubt, however, but that both the primary assumptions are incorrect. The muriatic

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* Philosophical Transactions, vol. lxxi. lxxii. lxxiii.

acid, even in the gaseous state, holds dissolved a portion of water, which it is not easy to estimate, and which it does not retain, at least uniformly, in its combinations; and were it even admitted to be the real acid, this could lead to no conclusion as to the proportion of real acid, in the other acids; since the hypothesis Mr Kirwan assumed is not just, that the same quantities of different acids will be spent in the saturation of potassa, but the reverse even is established by experiment, every base requiring different quantities of the various acids for its saturation.

Mr Kirwan himself was afterwards convinced of these errors, and conducted his investigations on different principles. There was still the difficulty of determining the strength of the acids, or what constituted the real acid in each; and Mr Kirwan found no other method than assuming that the sulphuric acid, which exists in sulphate of potassa, the nitric acid in nitrate of potassa, and the muriatic acid in muriate of potassa strongly dried, are the real acid. From observing the quantities of these acids of a certain specific gravity, which enter into the composition of these salts, he discovers the quantity of real acid, which the acids of these specific gravities contain. And, lastly, by discovering by experiment the quantities of the different acids of certain specific gravity, and the quantities of the different bases with which they combine, he determines the proportions of the different compound salts. He employs, at the same time, a peculiar method to discover what quantity of a compound salt is formed from given quantities of its elements combined together. The difficulty with regard to this always was to determine what proportion of water entered into its composition. The method employed by former chemists, was to obtain the salt in a crystallized state by evaporation of its solution, then to expose it to a red heat to expel the water of crystallization, and consider the remaining quantity as the real salt, formed of the acid and base alone. Mr Kirwan observes, that this method is liable to the objections, that many salts lose part of their acid, as well as their water, by such a heat, while others, from their strong attraction to water, may be capable of retaining a part of it at that temperature. The method he employed, therefore, was to saturate a known quantity of base with an acid, the specific gravity of which, and of course the quantity of real acid it contains, according to the preceding principles, are known. A solution is then prepared of a known quantity of the neutral salt, of the same species as that formed by saturation ; and the specific gravity of both solutions, at the same temperature, is examined, adding water to the stronger of the two, until their densities become equal. It is then inferred, that an equal proportion of salt exists in both ; but the proportion in one of them is known ; and therefore the proportion in the other, the weight of the whole being found, is also determined [*]. On these principles, the composition of the compound salts, given in the table (p. 288), was determined.

Though Mr Kirwan's investigations have been ably conducted, there are still very important objections to the results. The very basis of the investigation is doubtful,—the assumption, that it is real acid which exists in sulphate of potassa, nitrate of potassa, and muriate of potassa dried ; for it is possible, nay even probable, that in their dried state each of these salts may retain certain quantities of water ; and the tables of the quantity of real acid founded on this assumption, and serving as the basis of the individual experiments; may hence be incorrect. " A table of this construction," says Berthollet [†], " may be used to compare the quantities of acid, in the same species of acid, according to its different specific gravities, or the quantities of acid in a different species ; its utility is undoubted in many cases, but it does not appear to me to be useful for determining those elements of saline combinations, for which its author particularly intended it. It seems, that its use in this case has no superiority over the direct method employed by chemists : in effect it is always requisite to begin by determining the proportion of the base ; after that, it is either saturated by a quantity of acid, the real acid of which is given in Kirwan's table, or the process goes on to crystallization, and then to a strong desiccation, to ascertain the quantity of water which heat is capable of separating from the combination; the weight which the base has acquired and retains, notwithstanding the heat, is then considered as the real acid, and that lost by the combination during its desiccation, is considered as water; but as the determination of the water is always useful, chemists can seldom dispense with this last proof; nothing now remains but to know, whether it is proper to depend upon the table of Kirwan, or to consider as real acid, the weight acquired by a well-determined base, and retained by it after strong desiccation: it appears to me, that there is at least as much exactness in trusting to this augmentation of weight; for Kirwan's table only fixes the quantity of real acid by an examination made with a base: it therefore has, of necessity, all the uncertainty of this determination, and also, all those arising from a determination founded on a multiplicity of data."

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[*] Transactions of the Irish Academy, vol. iv. and vii.

[†] Chemical Statics, vol. i. p. 82.

These observations must be allowed to be so far just; and although both from the comparative superiority of Mr Kirwan's method, (defective though it may be to a certain extent), and from his being aware of a number of sources of error not attended to in former experiments, the proportions he assigns to the compound salts may be regarded as more accurate than those of his predecessors, they can be considered only as approximations; and this important part of the details of chemistry will still require further research.

I have already taken notice (Note A *g*. vol. i.) of the mode of verification ingeniously conceived by Guyton, and by which only can the accuracy of the proportions of neutral salts assigned by any method be determined,—that of mixing two salts together in a state of solution, which give rise to double decomposition; observing whether the result is an excess of acid, an excess of base, or precise neutralization in the new compounds; and then by a reference to the assigned proportions of the constituent principles of the salts mixed, and of the salts produced, discovering whether the state produced in the experiment is that which ought to occur according to these proportions. I have given an example from Guyton's memoir, applied to the proportions assigned by Kirwan in his former tables, in which their inaccuracy is shewn by this method. And I have remarked, that Berthollet, on applying this mode to the proportions given by Mr Kirwan in his last tables, found them equally at variance with the results of experiment. Thus, to take a single example; according to these tables, sulphate of potassa contains 82.48 of acid to 100 of base, sulphate of barytes 50 to 100, muriate of barytes contains 31.8 of acid to 100 of base, and muriate of potassa contains 56.30 of acid to 100 of base. When an exchange of bases, therefore, takes place on mixing solutions of muriate of barytes and sulphate of potassa, what is requisite to produce that exact neutralization which is the result? It is necessary that there should be a quantity of muriatic acid sufficient to saturate 100 parts of potassa, that is, 56.3 parts. But 56.3 parts of muriatic acid, according to the above proportions, would saturate 177.04 of barytes. This quantity of barytes requires, according to the table, for its saturation, 88.52 of sulphuric acid; but in the quantity of sulphate of potassa, which, according to the above data, can be decomposed, there are only 82.48 parts of sulphuric acid. Hence that result, according to these proportions, cannot be exact neutralization. But as this is actually the result, the proportions are wrong. Taking the proportions in the other salts as they have been assigned, it would be necessary to suppose in the muriate of barytes 164.96 of base, instead of 177.04, united with 56.30 of muriatic acid. Other examples might be given, but this is sufficient for illustration.

I have likewise already stated the conclusion to which the fact, that in these cases of complex affinity the state of neutralization still remains, leads,—that the different acids follow correspondent proportions with the different alkaline bases to produce this neutral state, so that if the proportion with regard to one be discovered, those of the others may be inferred. All that will be necessary, says Berthollet, will be to determine "the proportions of an acid with the different alkaline bases; it will then be sufficient to ascertain the proportions of a single combination of each of the other acids with an alkaline base, taking that which is the most convenient for experiment, and an easy calculation will give the proportions of all the others." This affords a method not difficult, and which would have the important advantage of giving results which might be received as accurate. The phosphoric or the boracic acid, and among the bases barytes and strontites, would afford substances which in such an investigation might be employed free from all source of error, as they can be obtained solid uncombined with water, and in a pure, and consequently an uniform state.

END OF VOL. II.